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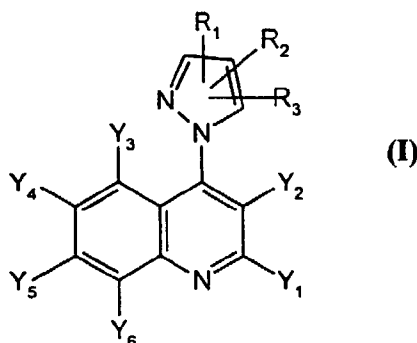
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(54) Title: 1-(QUINOLIN-4-YL)-1H-PYRAZOLE DERIVATIVES AND THEIR USE AS FUNGICIDES

(54) Titre: DERIVES DE 1-(QUINOLIN-4-YL)-1H-PYRAZOLE ET LEUR UTILISATION COMME FONGICIDES



(57) Abstract: The invention concerns compounds of general formula (I) wherein R₁, R₂, are different, their use as fungicides, in particular in the form of fungicidal compositions, and the methods for controlling phytopathogenic fungi using said compounds and compositions.

(57) Abrégé: Composés de formule générale (I) dans laquelle R₁ et R₂ sont différents leur procédé de préparation, leur utilisation comme fongicides, notamment sous forme de compositions fongicides, ainsi que les procédés de contrôle des champignons phytopathogènes des cultures à l'aide de ces composés ou de ces compositions.

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DERIVES DE 1-(QUINOLIN-4-YL)-1H-PYRAZOLE ET LEUR UTILISATION COMME FONGICIDES

5 **Domaine de l'invention**

[0001] La présente invention concerne de nouveaux composés comportant un groupe pyrazole, leur procédé de préparation, leur utilisation comme fongicides, notamment sous forme de compositions fongicides, ainsi que les procédés de
10 contrôle des champignons phytopathogènes des cultures à l'aide de ces composés ou de ces compositions.

État de la technique

15 [0002] Des très nombreux composés comportant un groupe pyrazole sont déjà connus et largement illustrés dans la littérature. À titre d'exemple, le brevet US 4,622,330 décrit des dérivés du pyrazole possédant des activités anti-parasitaires.

Plus spécifiquement, les brevets US 5,760,056 et WO-A-97/17064 décrivent des dérivés de quinolyl-pyrazoles possédant un groupement adamantylcarboxylique
20 et utiles dans le traitement thérapeutique de troubles du système nerveux central.

Les demandes de brevets EP-A-0703234 et DE-A-19636509 décrivent notamment des composés fongicides possédant une structure quinolyl-pyrazole dont le cycle pyrazole porte éventuellement un seul substituant.

25 [0003] Les dérivés connus de quinolyl-pyrazoles, et notamment ceux connus pour leur activité fongicide, présentent cependant de nombreux inconvénients, bien connus de l'utilisateur de tels composés, c'est-à-dire celui confronté aux problèmes de lutte contre les maladies fongiques des plantes : faible activité, composés efficaces sur une relativement faible gamme de maladies fongiques, faible sélectivité, toxicité, voire
30 écotoxicité.

Autrement dit, les composés fongicides connus sont faiblement actifs et/ou possèdent un spectre d'activité relativement étroit. Afin d'éradiquer toutes les différentes espèces de champignons s'attaquant aux plantes, l'utilisateur doit par exemple utiliser plusieurs produits, dont il doit connaître exactement le spectre et les
35 doses d'application. L'utilisation de plusieurs produits va de plus à l'encontre des modes de traitement des cultures préconisés aujourd'hui, où les doses d'application doivent être les plus faibles possible, dans le but évident de protection de l'environnement.

De plus, l'emploi de grandes quantités de produits et/ou de plusieurs produits fongicides différents sont bien souvent nuisibles aux cultures (toxicité des produits).

5 L'emploi de grandes quantités de produits dans le traitement des maladies fongiques entraîne dans certains cas l'apparition de souches fongiques résistantes à ces produits. C'est la raison pour laquelle il est toujours nécessaire de proposer à l'utilisateur de nouvelles molécules anti-fongiques.

10 [0004] Un objet de la présente invention est de proposer une nouvelle famille de composés ayant un large spectre d'action sur les champignons phytopathogènes des cultures.

Un autre objet de la présente invention est de proposer une nouvelle famille de composés ayant un large spectre d'action sur les champignons phytopathogènes des cultures permettant de résoudre les problèmes spécifiques rencontrés.

15 Un autre objet de la présente invention est de proposer une nouvelle famille de composés actifs à faibles doses sur les champignons phytopathogènes des cultures.

Un autre objet de la présente invention est de proposer une nouvelle famille de composés ayant un large spectre d'action amélioré sur les champignons phytopathogènes des cultures.

20 Un autre objet de la présente invention est de proposer une nouvelle famille de composés ayant un large spectre d'action amélioré sur les champignons phytopathogènes des cultures et possédant une toxicité et/ou une écotoxicité réduite.

25 Un autre objet de la présente invention est de proposer une nouvelle famille de composés ayant un large spectre d'action amélioré sur les champignons phytopathogènes des cultures comme les céréales, le riz, le maïs, le tournesol, les arbres fruitiers, les arbres forestiers, la vigne, les cultures oléagineuses, les cultures maraîchères, les solanées, la betterave, etc.

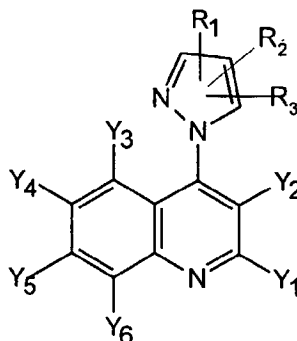
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Définition générale de l'invention :

[0005] De façon tout à fait surprenante, il a été trouvé que ces objets peuvent être réalisés en totalité ou en partie, par des composés comportant un motif quinolyl-pyrazole, dans lequel le pyrazole comporte au moins deux substituants différents.

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[0006] La présente invention concerne des composés de formule générale (I) :



composés de formule (I) dans laquelle :

- 5 • R₁ et R₂ sont différents et sont choisis parmi un radical alkyle, alkoxy, alkylthio, alkylsulfinyle, alkylsulfonyle, alkoxysulfonyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkénylcarbonyle, alkynylcarbonyle, alkylcarbonyloxy, alkénylcarbonyloxy, alkynylcarbonyloxy, alkoxy carbonyle, alkoxyalkylcarbonyle, alkényloxy carbonyle, alkynyloxy carbonyle, cycloalkyl-carbonyle, hétérocyclylcarbonyl, cycloalkyl-oxycarbonyle, cycloalkylalkyloxy carbonyle, hétérocyclyl-oxycarbonyle, hétérocyclylalkoxy carbonyle, thioalkylthiocarbonyle, alkoxythiocarbonyle, thioalkyle,
- 10 un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle, le radical hydroxy, le radical mercapto, le radical carboxy, le radical nitro, le radical cyano, le radical thiocyanato, le radical azido, un radical NR₄R₅, C(=O)NR₄R₅, C(=S)NR₄R₅, un radical C(=NR₄)R₅, un atome d'halogène,
- 15 le radical sulfonyle, le radical sulfinyle, le radical sulfanyle, le radical phosphoryle et le radical phosphone,
- ou bien,
- 20 R₁ et R₂ peuvent former ensemble un cycle de 4 à 7 atomes, contenant 2 à 3 atomes d'oxygène et/ou d'azote, éventuellement substitué par un ou plusieurs radicaux choisis parmi halogène, alkyle, haloalkyle, alkoxy, amino et NR₄R₅ ;
- 30 • R₃ est choisi parmi l'hydrogène, un radical alkyle, alkoxy, alkylthio, alkylsulfinyle, alkylsulfonyle, alkoxysulfonyle, alkényle, alkynyle,

- 5 alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cycloalkyle, hétérocyclyle, cycloalkylcarbonyle, hétérocyclylcarbonyl, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkénylcarbonyle, alkynylcarbonyle, alkylcarbonyloxy, alkénylcarbonyloxy, alkynylcarbonyloxy,
- 10 alkoxycarbonyle, alkényloxycarbonyle, alkynyloxycarbonyle, cycloalkyl-oxycarbonyle, cycloalkylalkyloxycarbonyle, hétérocyclyloxycarbonyle, hétérocyclylalkoxycarbonyle, un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle, le radical hydroxy, le radical mercapto, le radical carboxy, le radical nitro, le radical cyano, le radical thiocyanato, le radical azido, un radical NR_4R_5 , $\text{C}(=\text{O})\text{NR}_4\text{R}_5$, $\text{C}(=\text{S})\text{NR}_4\text{R}_5$, et un radical $\text{C}(=\text{NR}_4)\text{R}_5$,
- 15 R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical alkyle, alkoxy, alkylthio, alkylsulfinyle, alkylsulfonyle, alkoxyulfonyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cyanoalkyle, alkoxyalkyle, alkoxycarbonylalkyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkénylcarbonyle, alkynylcarbonyle, alkoxycarbonyle, alkényloxycarbonyle, alkynyloxycarbonyle, cycloalkyloxycarbonyle,

20 cycloalkylalkyloxycarbonyle, hétérocyclyloxycarbonyle, hétérocyclylalkoxycarbonyle, un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle, arylalkyle, hétéroarylalkyle, le radical mercapto, le radical carboxy, le radical nitro, le radical cyano, le radical thiocyanato, le radical azido, un radical OR_6 , amino, alkylamino, dialkylamino, aminoalkyle, alkylaminoalkyle et dialkylaminoalkyle, hydrazino,

25 ou bien, R_4 et R_5 peuvent former ensemble un cycle de 4 à 7 atomes, contenant 2 à 3 atomes d'oxygène et/ou d'azote, éventuellement substitué par un ou plusieurs radicaux choisis parmi halogène, alkyle, haloalkyle, alkoxy, amino et NR_7R_8 ;
 - 35 R_6 représente l'hydrogène, un radical alkyle, aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, cycloalkyle, cycloalkylalkyle, hétérocyclyle, hétérocyclyalkyle et alkoxycarbonylalkyle,

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• R_7 et R_8 , identiques ou différents, sont choisis parmi l'hydrogène, un radical alkyle, alkoxy, alkylthio, alkylsulfinyle, alkylsulfonyle, alcoxysulfonyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cyanoalkyle, alkoxyalkyle, alkoxycarbonylalkyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkénylcarbonyle, alkynylcarbonyle, alkoxycarbonyle, alkényloxycarbonyle, alkynyloxycarbonyle, cycloalkyloxycarbonyle, cycloalkylalkyloxycarbonyle, hétérocycliloxycarbonyle, hétérocyclylalkoxycarbonyle, un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle, arylalkyle, hétéroarylalkyle, le radical mercapto, le radical carboxy, le radical nitro, le radical cyano, le radical thiocyanato, le radical azido, un radical OR_6 , amino, alkylamino, dialkylamino, aminoalkyle, alkylaminoalkyle et dialkylaminoalkyle, hydrazino,

ou bien,

20
 R_7 et R_8 peuvent former ensemble un cycle de 4 à 7 atomes, contenant 2 à 3 atomes d'oxygène et/ou d'azote, éventuellement substitué par un ou plusieurs radicaux choisis parmi halogène, alkyle, haloalkyle, alkoxy et amino ;

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• les radicaux Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont choisis indépendamment les uns des autres parmi l'atome d'hydrogène, un atome d'halogène; le radical hydroxy, mercapto, nitro, thiocyanato, azido, cyano ou pentafluorosulfonyl, un radical alkyle, haloalkyle, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyle, haloalkoxyalkyle, alkylthioalkyle, haloalkylthioalkyle, cyanoalkyle, cyanoalkoxy, cyanoalkylthio, alkylsulfinyle, haloalkylsulfinyle, alkylsulfonyl, haloalkylsulfonyl, alcoxysulfonyl,

un groupe cycloalkyle, halocycloalkyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio,

un radical aryle ou hétéroaryle éventuellement substitué,

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 un radical amino, N-alkylamino, N,N-dialkylamino, acylamino, aminoalkyle, N-alkylaminoalkyle, N,N-dialkylaminoalkyle, acylaminoalkyle,

le radical carboxy, le radical carbamoyle, un radical N-alkylcarbamoyle, N,N-dialkylcarbamoyle, alkoxycarbonyle et un radical alkylcarbonyle,

ou bien

5 deux radicaux adjacents choisis parmi Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 pouvant également former, ensemble et avec les deux atomes de carbone qui les portent, un cycle aromatique à 6 chaînons, ou

deux radicaux adjacents choisis parmi Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 pouvant également former ensemble un radical divalent méthylène-di-oxy ;

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• l'ensemble des radicaux définis ci-dessus et possédant une chaîne hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle, alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, mercapto, NR_4R_5 , cyano, nitro, alkyle, alkoxyalkyle, aryle, hétéroaryle, halogène, alkoxy, alkylthio, alkylcarbonyle, alkylcarbonyloxy, alkénylcarbonyle, alkénylcarbonyloxy, alkynylcarbonyle, alkynylcarbonyloxy, arylcarbonyl, arylcarbonyloxy, hétéroarylcarbonyl, hétéroarylcarbonyloxy, aryloxy, arylthio, hétéroaryloxy, hétéroarylthio, halogénoalkoxy, perhalogénoalkoxy, cyanoalkylcarbonyloxy, cycloalkyle, hétérocyclyle, cycloalkylcarbonyle, cycloalkylcarbonyloxy, hétérocyclylcarbonyle, hétérocyclylcarbonyloxy, aryloxyalkylcarbonyloxy, alkylcarbonylalkylcarbonyloxy, alkoxycarbonylalkylcarbonyloxy, arylcarbonylcarbonyloxy, hétéroarylcarbonylcarbonyloxy, alkoxyalkoxyalkylcarbonyloxy et alkylthioalkylcarbonyloxy,

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• l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, mercapto, oxo, cyano, nitro, cyanato, thiocyanato, formyle, propylène-diyle, amino, alkylamino, dialkylamino, pentafluorosulfonyl, aryle, hétéroaryle, halogène, alkyle, haloalkyle, perhaloalkyle, alkényle, alkynyle, alkoxy, alkylthio, haloalkoxy, perhaloalkoxy, alkoxyalkyle, alkylcarbonyle, alkoxycarbonyle, alkylcarbonyloxy, alkénylcarbonyle, alkénylcarbonyloxy, alkynylcarbonyle, alkynylcarbonyloxy, arylcarbonyl, arylcarbonyloxy, hétéroarylcarbonyle, hétéroarylcarbonyloxy, aryloxy, arylthio, hétéroaryloxy, hétéroarylthio, cycloalkyle, hétérocyclyle, cycloalkylcarbonyle et hétérocyclylcarbonyle,

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leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles formes tautomères,

ainsi que les sels, les N-oxydes et les complexes métalliques et métalloïdiques des composés de formule (I) tels qu'ils viennent d'être définis.

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[0007] Dans les définitions précédentes des radicaux R_1 à R_8 et Y_1 à Y_6 , il doit être compris que :

- 10 - les radicaux ou groupements alkyle, alkényle, alkynyle, (ainsi que les radicaux dérivés, comme alkoxy, alkoxy-carbonyle, etc.) comportent de 1 à 6 atomes de carbone (de 2 à 6 pour les radicaux alkényle et alkynyle) en chaîne linéaire ou ramifiée ;
- les radicaux cycloalkyle contiennent de 3 à 7 atomes de carbone, les cycles étant partiellement ou totalement saturés, par exemple cyclopropyle, cyclopentyle, cyclopentényle, cyclohexyle, cyclohexényle ;
- 15 - les radicaux hétérocyclyle contiennent de 3 à 7 atomes, parmi lesquels 1, 2 ou 3 sont choisis parmi azote, oxygène et soufre, les autres étant des atomes de carbone, les cycles étant partiellement ou totalement saturés, par exemple aziridyle, morpholyle, thiomorpholyle, pipéridyle, pipérazinyle, pyrrolidinyle, imidazolidinyle, thioimidazolidinyle, isoxazolyle,
- 20 isothiazolyle, tétrahydropyridinyle, 1,3-dioxolyle ;
- par radical aryle, on entend le radical phényle ou le radical naphthyle ;
- par radical hétéroaryle, on entend un radical hétéroaromatique mono ou bicyclique de 3 à 10 chaînons pouvant comporter jusqu'à 3 hétéroatomes identiques ou différents et choisis parmi azote, oxygène et soufre. Des
- 25 exemples de radicaux aromatiques sont le radical pyridyle, quinolyle, quinoxalyle, furyle, thiényle, pyrrolyle, pyrazinyle, pyridazinyle,

[0008] Par ailleurs, les termes génériques suivants sont utilisés avec les significations suivantes :

- 30 - halogène signifie fluor, chlore, brome ou iode ;
- les radicaux halogénés peuvent comporter un ou plusieurs atomes d'halogènes identiques ou différents ;
- le radical acyle signifie alkylcarbonyle, ou cycloalkylcarbonyle ;
- lorsqu'un radical est disubstitué, les deux substituants peuvent être
- 35 identiques ou différents ;
- lorsque le radical amino est disubstitué, les deux substituants peuvent constituer un hétérocycle azoté saturé ou insaturé, de 4 ou 6 atomes ;

- lorsque le radical carbamoyle est disubstitué, les deux substituants peuvent constituer un hétérocycle azoté saturé ou insaturé, de 4 ou 6 atomes ;

[0009] Des modes de réalisations préférés de l'invention sont ceux où les produits de formule (I) présentent en outre l'une et/ou l'autre des caractéristiques suivantes prises isolément ou en combinaison :

- R_1 et R_2 sont différents et sont choisis parmi un radical alkyle, alkoxyalkyle, alkylthioalkyle, hydroxyalkyle, aminoalkoxyalkyle, N-alkylaminoalkoxy-alkyle, N,N-dialkylaminoalkoxyalkyle, aminoalkylthioalkyle, N-alkyl-aminoalkyl-thioalkyle, N,N-dialkylaminoalkylthioalkyle, alkényle, cycloalkyle, cycloalkylcarbonyle, hétérocyclcarbonyl, hétérocyclyle, cycloalkylalkyle, hétérocyclalkyle, alkylcarbonyle, alkylcarbonyloxy, alkylcarbonyloxyalkyle, alkénylcarbonyloxyalkyle, alkynylcarbonyloxyalkyle, alkoxycarbonyle, cycloalkylalkoxycarbonyle,

un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, aryloxyalkyle, hétéroaryloxyalkyle, arylcarbonyle, hétéroarylcarbonyle, arylcarbonyloxy-alkyle, hétéroarylcarbonyloxyalkyle,
le radical hydroxy, le radical carboxy, le radical nitro, le radical cyano, un radical NR_4R_5 , $CH_2NR_4R_5$, $C(=O)NR_4R_5$, et un radical $C(=NR_4)R_5$,

- R_3 est choisi parmi l'hydrogène, un radical alkyle, alkoxy, alkoxyalkyle, alkylthio, alkényle, alkynyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclalkyle, alkylcarbonyle, alkylcarbonyloxy, alkoxycarbonyle,

le radical hydroxy, le radical mercapto, le radical carboxy, et un radical NR_4R_5 ,

- R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical alkyle, alkoxy, alkoxyalkyle, alkylthio, alkényle, alkynyle, alkényloxy, alkynyloxy, cyanoalkyle, alkoxyalkyle, alkoxycarbonylalkyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclalkyle, alkylcarbonyle, alkoxycarbonyle,

un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle,
le radical mercapto, le radical cyano, un radical OR_6 , amino, alkylamino, dialkylamino, aminoalkyle, alkylaminoalkyle et dialkylaminoalkyle,

- R_6 représente l'hydrogène, un radical alkyle, aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, cycloalkyle, cycloalkylalkyle, hétérocyclyle, hétérocyclyalkyle, et alkoxycarbonylalkyle,
- 5 les radicaux Y_1, Y_2, Y_3, Y_4, Y_5 et Y_6 sont choisis indépendamment les uns des autres parmi l'atome d'hydrogène, un atome d'halogène, le radical hydroxy, mercapto, nitro, cyano ou pentafluorosulfonyl, un radical alkyle, haloalkyle, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyle, haloalkoxyalkyle, cyanoalkyle, cyanoalkoxy, cyanoalkylthio,

10 un radical alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, un radical amino, N-alkylamino, N,N-dialkylamino, aminoalkyle, N-alkylaminoalkyle, N,N-dialkylaminoalkyle,

15 le radical carboxy, alkoxycarbonyl et un radical alkylcarbonyl,

ou bien

deux radicaux adjacents choisis parmi Y_1, Y_2, Y_3, Y_4, Y_5 et Y_6 pouvant également former, ensemble et avec les deux atomes de carbone qui les

20 portent, un cycle aromatique à 6 chaînons,
- l'ensemble des radicaux définis ci-dessus et possédant une chaîne hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle, alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs

25 groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, mercapto, amino, N-alkylamino, N,N-dialkylamino, cyano, nitro, aryle, hétéroaryle, halogène, alkoxy, alkylthio, aryloxy, arylthio, hétéroaryloxy, hétéroarylthio, halogénoalkoxy, perhalogénoalkoxy, cyanoalkylcarbonyloxy, cycloalkyle, hétérocyclyle, cycloalkylcarbonyl,

30 cycloalkylcarbonyloxy, hétérocyclylcarbonyl, hétérocyclylcarbonyloxy, aryloxyalkylcarbonyloxy, alkylcarbonylalkylcarbonyloxy, alkoxycarbonylalkylcarbonyloxy, arylcarbonylcarbonyloxy, hétéroarylcarbonylcarbonyloxy, alkoxyalkoxyalkylcarbonyloxy et alkylthioalkylcarbonyloxy,
- l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent

35 éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi oxo, cyano, nitro, formyle, propylène-diyle, amino, N-alkylamino, N,N-dialkylamino, aryle,

hétéroaryle, halogène, alkyle, haloalkyle, perhaloalkyle, alkoxy, alkylthio, haloalkoxy, perhaloalkoxy, alkoxyalkyle, alkylcarbonyle, alkoxycarbonyle, aryloxy, cycloalkyle et hétérocyclyle,

5 leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles formes tautomères,

ainsi que les sels, les N-oxydes et les complexes métalliques et métalloïdiques des composés de formule (I) tels qu'ils viennent d'être définis.

10 [0010] De manière avantageuse, on préfère encore les composés de formule (I) possédant les caractéristiques suivantes prises isolément ou en combinaison :

- R_1 et R_2 sont différents et sont choisis parmi un radical alkyle, alkoxyalkyle, alkylthioalkyle, hydroxyalkyle, aminoalkoxyalkyle, N-alkylaminoalkoxy-alkyle, N,N-dialkylaminoalkoxyalkyle, aminoalkyl-
15 thioalkyle, N-alkylaminoalkyl-thioalkyle, N,N-dialkylaminoalkylthioalkyle, alkényle, cycloalkylcarbonyle, hétérocyclylcarbonyl, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkylcarbonyloxy, alkylcarbonyl-oxyalkyle, alkoxycarbonyle, cycloalkylalkoxycarbonyle, un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, aryloxyalkyle, hétéroaryloxyalkyle, arylcarbonyle, hétéroarylcarbonyle,
20 le radical carboxy, un radical NR_4R_5 , $CH_2NR_4R_5$, $C(=O)NR_4R_5$, et un radical $C(=NR_4)R_5$,
- R_3 est choisi parmi l'hydrogène, un radical alkyle, alkoxy, alkoxyalkyle, alkylthio, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle, alkoxycarbonyle,
25 le radical carboxy, et un radical NR_4R_5 ,
- R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical alkyle, alkoxy, alkoxyalkyle, alkoxyalkyle, alkoxycarbonylalkyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle,
30 un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, et un radical OR_6 ,
- R_6 représente l'hydrogène, un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, cycloalkyle, cycloalkylalkyle, hétérocyclyle, et hétérocyclylalkyle,
35

- 5 les radicaux Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont choisis indépendamment les uns des autres parmi l'atome d'hydrogène, un atome d'halogène, le radical hydroxy, un radical alkyle, haloalkyle, alkoxy, haloalkoxy, alkoxyalkyle et haloalkoxyalkyle,
 - 10 l'ensemble des radicaux définis ci-dessus et possédant une chaîne hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle, alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, halogène, alkoxy et halogénoalkoxy,
 - 15 l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi oxo, halogène, alkyle, haloalkyle, perhaloalkyle, alkoxy, haloalkoxy, perhaloalkoxy, alkoxyalkyle, alkylcarbonyl, alkoxycarbonyl et aryloxy,
- 20 leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles formes tautomères,
- ainsi que les sels, les N-oxydes et les complexes métalliques et métalloïdiques des composés de formule (I) tels qu'ils viennent d'être définis.
- [0011] De manière particulièrement avantageuse, on préfère encore les composés
- 25 de formule (I) possédant les caractéristiques suivantes prises isolément ou en combinaison :
- 30 R_1 et R_2 sont différents et sont choisis parmi un radical alkyle, alkoxyalkyle, hydroxyalkyle, cycloalkylcarbonyl, hétérocyclalcarbonyl, alkylcarbonyl, alkylcarbonyloxy, alkylcarbonyloxyalkyle, alkoxycarbonyl, cycloalkylalkoxycarbonyl, un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, aryloxyalkyle, hétéroaryloxyalkyle, le radical carboxy et un radical $C(=O)NR_4R_5$,
 - 35 R_3 représente l'hydrogène,
 - R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical

alkyle, alkoxy et alkoxycarbonylalkyle,

- les radicaux Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont choisis indépendamment les uns des autres parmi l'atome d'hydrogène, un atome d'halogène, un radical alkyle, haloalkyle et alkoxy,
- l'ensemble des radicaux définis ci-dessus et possédant une chaîne hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle, alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, halogène, alkoxy et haloalkoxy,
- l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi oxo, halogène, alkyle, haloalkyle, alkoxy, haloalkoxy, perhaloalkoxy et alkoxycarbonyle,

leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles formes tautomères,

ainsi que les sels, les N-oxydes et les complexes métalliques et métalloïdiques des composés de formule (I) tels qu'ils viennent d'être définis.

[0012] On préfère enfin les composés de formule (I) choisis parmi le ou la :

- 1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
- 3-(méthoxyméthyl)-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazole-4-carboxylate de méthyle ;
- 1-(7-chloro-4-quinolyl)-5-(3-nitrophényl)-1*H*-pyrazole-4-carboxylate de méthyle ;
- 1-(7-chloro-4-quinolyl)-*N,N*-diéthyl-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolyl)-*N*-méthoxy-5-(méthoxyméthyl)-*N*-méthyl-1*H*-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolyl)-5-(2-méthoxyéthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
- 5-(2-méthoxyéthyl)-1-(7-méthoxy-4-quinolyl)-1*H*-pyrazole-4-carboxylate de méthyle ;

- 1-[2,8-bis(trifluorométhyl)-4-quinolyl]-*N*-méthoxy-3-(méthoxyméthyl)-*N*-méthyl-1*H*-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolyl)-3-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
- 5 • 1-(6-fluoro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
- 1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de 2-éthoxyéthyle ;
- *N*-méthoxy-3-(méthoxyméthyl)-*N*-méthyl-1-[8(trifluorométhyl)-4-quinolyl]-1*H*-pyrazole-4-carboxamide ;
- 10 • [1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-yl](1,3-thiazolidin-3-yl)méthanone ;
- 2-[1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazol-4-yl]-2-propanol ;
- 15 • 1-(7-chloro-4-quinolyl)-*N*-méthoxy-5-(méthoxyméthyl)-*N*-propyl-1*H*-pyrazole-4-carboxamide ;
- 5-({4-méthoxycarbonyl}-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazol-5-yl)méthoxy)isophtalate de diméthyle ;
- 1-(7-chloro-4-quinolyl)-*N*-isopropyl-*N*-méthoxy-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxamide ;
- 20 • 4-[[1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-yl]carbonyl](méthoxy)amino]butanoate de méthyle ;
- 5-[(heptanoyloxy)méthyl]-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazole-4-carboxylate de méthyle ;
- 25 • la 7-chloro-4-{5-méthoxyméthyl}-4-[5-trifluorométhyl]-1,2,4-oxadiazol-3-yl]-1*H*-pyrazol-1-yl} ;quinoléine
- methyl 1-(7-chloro-4-quinolyl)-5-[[1-(1-diméthylethyl)sulfanyl]methyl]-1*H*-pyrazole-4-carboxylate ;
- 1-(7-chloro-4-quinolyl)-5-[(méthoxy)méthyl]-1*H*-pyrazole-4-carbaldehyde ;
- 30 • [1-(7-chloro-4-quinolyl)-4-(1-phenylethényl)-1*H*-pyrazol-5-yl]methyl methyl ether ;
- 1-{3-[(méthoxy)méthyl]-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazol-4-yl}éthanone ;
- 35 • methyl 3-[(méthoxy)méthyl]-5-(methylsulfanyl)-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazole-4-carboxylate ;
- methyl 5-chloro-3-[(méthoxy)méthyl]-1-[8-(trifluorométhyl)-4-

- quinoliny]-1H-pyrazole-4-carboxylate ;
- (1E)-1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanone oxime ;
 - 1-(2 ;7-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-
5 [(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - N-methyl-1-[2-methyl-8-(1-methylethyl)-4-quinoliny]-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-[2-methyl-7-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
 - 10 • N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-(2 ;5 ;7-trimethyl-4-quinoliny)-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-2 ;8-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 1-(6 ;8-dichloro-2-methyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-
15 [(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-(8-methyl-4-quinoliny)-1H-pyrazole-4-carboxamide ;
 - 1-(2 ;8-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 20 • N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-[2-methyl-8-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
 - 1-(6-chloro-2 ;8-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-(2-methyl-4-
25 quinoliny)-1H-pyrazole-4-carboxamide ;
 - N-methyl-1-[2-methyl-8-(methyloxy)-4-quinoliny]-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-(2 ;6 ;8-trimethyl-4-quinoliny)-1H-pyrazole-4-carboxamide ;
 - 30 • 1-[5-chloro-2-methyl-8-(methyloxy)-4-quinoliny]-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 1-(5 ;7-dichloro-4-quinoliny)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 5-(hydroxymethyl)-N-methyl-N-(methyloxy)-1-[8-(trifluoromethyl)-4-
35 quinoliny]-1H-pyrazole-4-carboxamide ;
 - 1-(6-chloro-2 ;8-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-[2-(methyloxy)ethyl]-1H-pyrazole-4-carboxamide ;

- N-methyl-N-(methyloxy)-5-[2-(methyloxy)ethyl]-1-[8-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-5-[2-(methyloxy)ethyl]-1-[7-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- 5 • N ;5-dimethyl-N-(methyloxy)-1-[2-methyl-8-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbaldehyde O-methyloxime ;
- 5-(bromomethyl)-1-(5 ;7-dichloro-4-quinoliny)-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 10 • 1-(7-chloro-4-quinoliny)-3-(dibromomethyl)-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanol ;
- 15 • (1E)-1-{3-[(methyloxy)methyl]-1-[8-(trifluoromethyl)-4-quinoliny]-1H-pyrazol-4-yl}ethanone O-(cyclopropylmethyl)oxime ;
- N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-[7-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-[2-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- 20 • 1-(7-chloro-4-quinoliny)-N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- methyl 3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-4 ;5-dihydro-5-isoxazolecarboxylate ;
- 25 • 1-(7-chloro-4-quinoliny)-N-(cyclopropylcarbonyl)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- ethyl 3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-oxopropanoate ;
- 1-(7-chloro-4-quinoliny)-N-methyl-N-(methyldisulfanyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 30 • 1-(7-chloro-4-quinoliny)-N-(ethyldisulfanyl)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinoliny)-N-methyl-N-[(1-methylethyl)disulfanyl]-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 35 • ethyl 1-(7-chloro-4-quinoliny)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbimidothioate ;
- (1E)-1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-

- yl}-1-propanone O-methyloxime ;
- (3E)-4-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-buten-2-one ;
 - ethyl (2Z ;4E)-5-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-hydroxy-2 ;4-pentadienoate ;
 - 2-propenyl (2E)-3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-2-propenoate ;
 - 1-(7-chloro-4-quinolinyl)-N-(ethyloxy)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 4-(3-[(methyloxy)methyl]-4-{5-[(methyloxy)methyl]-3-isoxazolyl}-1H-pyrazol-1-yl)-8-(trifluoromethyl)quinoline ;
 - 7-chloro-4-{4-[(ethyloxy)methyl]-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}quinoline ;
 - (Z)-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}[(methyloxy)imino]methyl methanesulfonate ;
 - 1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-N-(methylsulfanyl)-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolinyl)-N-(ethylsulfanyl)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - {1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}acetonitrile ;
 - 3-(hydroxymethyl)-N ;N-dimethyl-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
 - {1-(7-chloro-4-quinolinyl)-4-[3-(4-fluorophenyl)-1 ;2 ;4-oxadiazol-5-yl]-1H-pyrazol-5-yl}methyl methyl ether ;
 - 1-(7-chloro-4-quinolinyl)-N-(methyloxy)-N ;5-bis[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - [1-(7-chloro-4-quinolinyl)-4-(3-phenyl-1 ;2 ;4-oxadiazol-5-yl)-1H-pyrazol-5-yl]methyl methyl ether ;
 - 2-oxiranylmethyl 1-(7-chloro-4-quinolinyl)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboximidoate ;
 - 1-(7-chloro-4-quinolinyl)-N'-[(cyclopropylmethyl)oxy]-5-[(methyloxy)methyl]-1H-pyrazole-4-carboximidamide ;
 - 1-(7-chloro-4-quinolinyl)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboximidoyl chloride ;
 - 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-N ;N-dimethyl-4 ;5-dihydro-5-isoxazolecarboxamide ;

- (1Z)-1-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanone O-(2-methylpropanoyl)oxime ;
- (1E)-1-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanone O-(cyclopropylcarbonyl)oxime ;
- 5 • 1-(8-fluoro-4-quinolinyl)-N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-(7-methyl-4-quinolinyl)-1H-pyrazole-4-carboxamide ;
- 10 • 1-(7-chloro-4-quinolinyl)-N-methyl-N-(methyloxy)-5-({[2-(methyloxy)-5-nitrophenyl]oxy}methyl)-1H-pyrazole-4-carboxamide ;
- 5-{{[2-bromo-3-pyridinyl]oxy}methyl}-N-methyl-N-(methyloxy)-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
- 5-{{[4'-bromo[1 ; 1'-biphenyl]-4-yl]oxy}methyl}-N-methyl-N-(methyloxy)-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
- 15 • 5-chloro-N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
- methyl {[({1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}carbonyl)(methyl)amino]oxy}(oxo)acetate ;
- 1-{1-(7-fluoro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-1-propanone ;
- 20 • (1E)-1-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanone O-[2-(methyloxy)acetyl]oxime ;
- 4-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}benzaldehyde ;
- 25 • 1-(7-chloro-4-quinolinyl)-5-({[2-(ethylsulfanyl)phenyl]oxy}methyl)-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-N-(propyloxy)-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-N-(2-propenyloxy)-1H-pyrazole-4-carboxamide ;
- 30 • 1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-N-[(1-methylpropyl)oxy]-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-methyl-N-[(1-methylethyl)oxy]-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 35 • methyl 4-{{[({1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}carbonyl)(methyl)amino]oxy}butanoate ;
- N-(3-butenyloxy)-1-(7-chloro-4-quinolinyl)-N-methyl-5-

- [(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-5-[(ethyloxy)methyl]-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 4-{4-{4 ;5-bis[(methyloxy)methyl]-3-isoxazolyl}-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}-7-bromoquinoline ;
- (3-{1-(6-fluoro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl acetate ;
- 4-{4-{4 ;5-bis[(methyloxy)methyl]-3-isoxazolyl}-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}-6-fluoroquinoline ;
- 7-ethyl-4-(5-[(methyloxy)methyl]-4-{5-[(tetrahydro-2H-pyran-2-yloxy)methyl]-3-isoxazolyl}-1H-pyrazol-1-yl)quinoline ;
- 4-{4-{4 ;5-bis[(methyloxy)methyl]-3-isoxazolyl}-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}-7-ethylquinoline ;
- 3-{[(3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl]oxy}propanenitrile ;
- methyl 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-4-methyl-5-isoxazolecarboxylate ;
- 1 ;1-dimethylethyl 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolecarboxylate ;
- 3-{[(3-{1-(7-ethyl-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl]oxy}propanenitrile ;
- {1-(7-chloro-4-quinolinyl)-4-[2-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}methyl methyl ether ;
- 7-chloro-4-(5-[(methyloxy)methyl]-4-{4-[(trifluoromethyl)oxy]phenyl}-1H-pyrazol-1-yl)quinoline ;
- methyl 5-[(methyloxy)methyl]-1-(6 ;7 ;8-trichloro-4-quinolinyl)-1H-pyrazole-4-carboxylate ;
- 1-(7-chloro-4-quinolinyl)-N-methyl-5-{[(1-methylethyl)oxy]methyl}-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- methyl 3-[(methyloxy)methyl]-5-(2-thienyl)-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxylate ;
- 7-chloro-4-(5-[(methyloxy)methyl]-4-{3-[(methyloxy)methyl]-1 ;2 ;4-oxadiazol-5-yl}-1H-pyrazol-1-yl)quinoline ;
- [1-(7-chloro-4-quinolinyl)-4-(1 ;3-thiazol-2-yl)-1H-pyrazol-5-yl]methyl methyl ether ;
- [1-(7-chloro-4-quinolinyl)-4-(4 ;5-dihydro-1 ;3-thiazol-2-yl)-1H-pyrazol-5-yl]methyl methyl ether ;

- 1 ;1-dimethylethyl 1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxylate ;
- 1-(7-cyano-4-quinolinyl)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 5 • [4-[5-(bromomethyl)-3-isoxazolyl]-1-(7-bromo-4-quinolinyl)-1H-pyrazol-5-yl]methyl methyl ether ;
- 1-(7-chloro-4-quinolinyl)-N'-methyl-5-[(methyloxy)methyl]-N'-phenyl-1H-pyrazole-4-carbohydrazide ;
- 1-(7-chloro-4-quinolinyl)-N'-(2 ;5-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
- 10 • 1-(7-chloro-4-quinolinyl)-N'-(1 ;1-dimethylethyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
- (1-(7-chloro-4-quinolinyl)-4-{[methyl(methyloxy)amino]carbonyl}-1H-pyrazol-5-yl)methyl 2-methylpropanoate ;
- 15 • N-ethyl-1-(6-fluoro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-(cyclopropylmethyl)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-4 ;6-dimethyl-4H-1 ;2 ;4-oxadiazin-5(6H)-one ;
- 20 • N-(4-chloro-2-butynyl)-1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- methyl 1-(7-chloro-4-quinolinyl)-5-(methyloxy)-1H-pyrazole-4-carboxylate ;
- 25 • 1-(7-chloro-4-quinolinyl)-5-(ethylsulfanyl)-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-N-(4-morpholinyl)-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-methyl-N-(methyloxy)-5-(methylsulfanyl)-1H-pyrazole-4-carboxamide ;
- 30 • (1-(7-chloro-4-quinolinyl)-4-{[methyl(methyloxy)amino]carbonyl}-1H-pyrazol-5-yl)methyl cyclopropanecarboxylate ;
- (1-(7-chloro-4-quinolinyl)-4-{[methyl(methyloxy)amino]carbonyl}-1H-pyrazol-5-yl)methyl 2-thienylacetate ;
- 35 • 7-chloro-4-(5-[(methyloxy)methyl]-4-{1-[3-(methyloxy)propyl]-1H-imidazol-5-yl}-1H-pyrazol-1-yl)quinoline ;
- [1-(7-chloro-4-quinolinyl)-4-(1-methyl-1H-imidazol-5-yl)-1H-pyrazol-5-

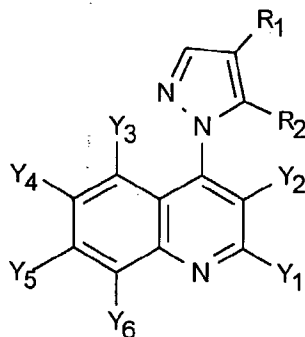
- yl)methyl methyl ether ;
- {1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}[(trimethylsilyl)oxy]acetonitrile ;
 - [1-(7-bromo-4-quinolinyl)-4-(1-piperidinylcarbonyl)-1H-pyrazol-5-yl)methyl methyl ether ;
 - methyl {4-(1-piperidinylcarbonyl)-1-[7-(trifluoromethyl)-4-quinolinyl]-1H-pyrazol-5-yl}methyl ether ;
 - 5-amino-1-(7-chloro-4-quinolinyl)-1H-pyrazole-4-carbonitrile ;
 - 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-2-thiophenecarbaldehyde ;
 - [1-(7-chloro-4-quinolinyl)-4-(5-ethenyl-1 ;3-oxazol-2-yl)-1H-pyrazol-5-yl)methyl methyl ether ;
 - 1-(2-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-1 ;3-oxazol-5-yl)ethyl acetate ;
 - [1-(7-bromo-4-quinolinyl)-4-(2-isoxazolidinylcarbonyl)-1H-pyrazol-5-yl)methyl methyl ether ;
 - {4-(2-isoxazolidinylcarbonyl)-1-[7-(trifluoromethyl)-4-quinolinyl]-1H-pyrazol-5-yl}methyl methyl ether ;
 - [1-(7-ethyl-4-quinolinyl)-4-(2-isoxazolidinylcarbonyl)-1H-pyrazol-5-yl)methyl methyl ether ;
 - [1-(6-fluoro-4-quinolinyl)-4-(2-isoxazolidinylcarbonyl)-1H-pyrazol-5-yl)methyl methyl ether ;
 - N'-(2-chlorophenyl)-1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinolinyl)-N'-(2 ;4-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinolinyl)-N'-(2 ;6-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-N'-(3-methylphenyl)-1H-pyrazole-4-carbohydrazide ;
 - N'-(3-chlorophenyl)-1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - N'-(3-chloro-4-methylphenyl)-1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinolinyl)-N'-(3 ;4-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinolinyl)-N'-(4-cyanophenyl)-5-[(methyloxy)methyl]-1H-

pyrazole-4-carbohydrazide ;

- (3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl phenyl sulfone ;
- (3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl ethyl sulfoxide ;
- [4-(4-chlorophenyl)-1-(7-chloro-4-quinoliny)-1H-pyrazol-5-yl]methyl methyl ether ;
- 1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-phenyl-2-propyn-1-one ;
- N-({1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}methyl)-3-(methyloxy)-1-propanamine,

ainsi que leurs éventuelles formes tautomères, leurs sels, N-oxydes et complexes métalliques et métalloïdiques.

[0013] Parmi les composés de formule (I) tels qu'ils viennent d'être définis, un groupe de composés particulièrement intéressants est constitué par les composés de formule générale (IV) :



- cas particulier des composés de formule (I) pour lesquels R_3 représente l'hydrogène et R_1 et R_2 sont respectivement en position 4 et 5 du noyau pyrazole, R_2 , Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 étant tels que définis précédemment, et R_1 représente un groupe carboxy, carbamoyle, N-alkylcarbamoyle, N,N-dialkylcarbamoyle, N-alkyl,N-alkoxyalkylcarbamoyle, N-alkoxycarbamoyle, N-alkyl-N-aminoalkylcarbamoyle, N,N-diaminoalkylcarbamoyle, alkoxycarbonyle inférieur; un nitrile, un groupe acyle inférieur.

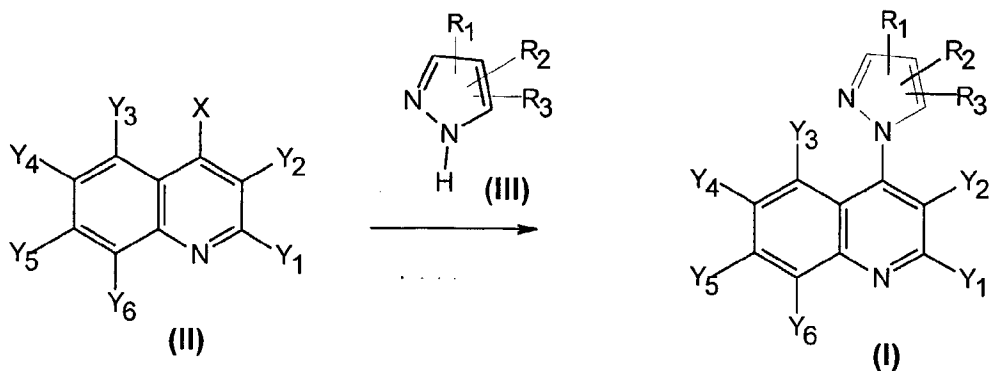
- [0014] Les composés de formules générales (I) et (IV) ainsi que les composés éventuellement utilisables à titre d'intermédiaires dans les procédés de préparation, et qui seront définis à l'occasion de la description de ces procédés, peuvent exister sous

une ou plusieurs formes d'isomères optiques ou chiraux selon le nombre de centres asymétriques du composé. L'invention concerne donc aussi bien tous les isomères optiques que leurs mélanges racémiques ou scalémiques (on désigne par scalémique un mélange d'énantiomères dans des proportions différentes), ainsi que les mélanges de tous les stéréoisomères possibles en toutes proportions. La séparation des diastéréoisomères et/ou des isomères optiques peut s'effectuer selon les méthodes connues en soi (E.Eliel ibid.).

[0015] La préparation des réactifs utilisés dans l'une ou l'autre des méthodes de préparation suivantes, est habituellement connue en soi et est habituellement décrite spécifiquement dans l'art antérieur ou d'une manière telle que l'homme de l'art peut l'adapter au but souhaité.

L'art antérieur utilisable par l'homme de l'art pour établir les conditions de préparation des réactifs, peut être trouvé dans de nombreux ouvrages généraux de chimie comme "Advanced Organic Chemistry" de J.March, Ed. Wiley (1992), "Methoden der organischen Chemie" (Houben-Weyl), Ed. Georg Thieme Verlag ou les "Chemical Abstracts" Ed. American Chemical Society ainsi que dans les bases de données informatiques accessibles au public.

[0016] Les composés de la présente invention de formules générales (I) et (IV) ainsi que les composés éventuellement utilisables à titre d'intermédiaires dans les procédés de préparation, peuvent être préparés selon le procédé suivant :



composés de formules (I), (II) et (III), dans lesquelles X représente un halogène et R_1 , R_2 , R_3 , Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont tels que définis précédemment,

la réaction étant effectuée en présence d'une base organique ou inorganique, en l'absence ou en présence d'un solvant.

[0017] Cette réaction est généralement effectuée à une température comprise entre

-80°C et 180°C (de préférence entre 0°C et 150°C) ou au point d'ébullition du solvant utilisé. Le solvant approprié pour cette réaction peut être un hydrocarbure aliphatique comme le pentane, l'hexane, l'heptane, l'octane ; un hydrocarbure aromatique comme le benzène, le toluène, les xylènes, les halogénobenzènes ; un éther comme le diéthyléther, le diisopropyléther, le tétrahydrofurane, le dioxane, le diméthoxyéthane ; un hydrocarbure halogéné comme le dichlorométhane, le chloroforme, le 1,2-dichloroéthane, le 1,1,1-trichloroéthane ; un ester comme l'acétate de méthyle, l'acétate d'éthyle, un nitrile comme l'acétonitrile, le propionitrile, le benzonitrile ; un solvant aprotique dipolaire comme la diméthylformamide, la diméthylacétamide, la N-méthylpyrrolidone, la diméthylproylèneurée, le diméthylsulfoxyde, ou l'eau. Des mélanges de ces différents solvants peuvent être aussi utilisés.

[0018] La durée réactionnelle dépend des conditions utilisées et est généralement comprise entre 0,1 à 48 h.

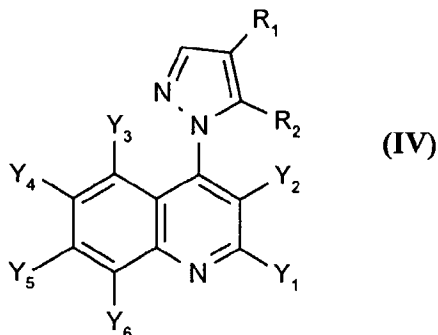
Il n'y a pas de limitation stricte pour les proportions relatives des composés de formule (II) et de formule (III). Il est cependant avantageux de choisir un rapport molaire (III) / (II) compris entre 0,1 et 10, de préférence 0,5 à 2.

[0019] Comme base organique ou inorganique appropriée pour cette réaction, on peut citer les hydroxydes de métaux alcalins et alcalino-terreux comme l'hydroxyde de sodium, de potassium, de césium ou de calcium ; les alcoolates de métaux alcalins et alcalino-terreux comme le tert-butylate de potassium, les hydrures de métaux alcalins et alcalino-terreux, comme l'hydruire de sodium, de potassium ou de césium ; les carbonates et bicarbonates de métaux alcalins et alcalino-terreux comme le carbonate de sodium, de potassium, de calcium ou le bicarbonate de sodium, de potassium ou de calcium ; les bases organiques, de préférences azotées, comme la pyridine, les alkylpyridines, les alkylamines comme la triméthylamine, la triéthylamine ou la di-isopropyléthylamine, les dérivés aza comme le 1,5-diazabicyclo[4.3.0]non-5-ène ou le 1,8-diazabicyclo[5.4.0]undec-7-ène, les phosphazènes comme le 1-terbutyl-2,2,4,4,4-pentakis-(diméthylamino)-2 λ^5 ,4 λ^5 -caténadi(phosphazène).

[0020] Pour des références sur cette réaction on peut citer : Advances in Heterocyclic Chemistry, Volume 6, pages 414-416, pour une référence très générale sur la préparation des composés de formule (III) on peut citer Houben-Weyl, band E8b, Hetarene III, Teil 2 pages 408-704, pour les composés de formule (II) on peut citer : Tetrahedron (1985) 41, 3033-3036 et Organic Synthesis, Col. Vol. 3, 272

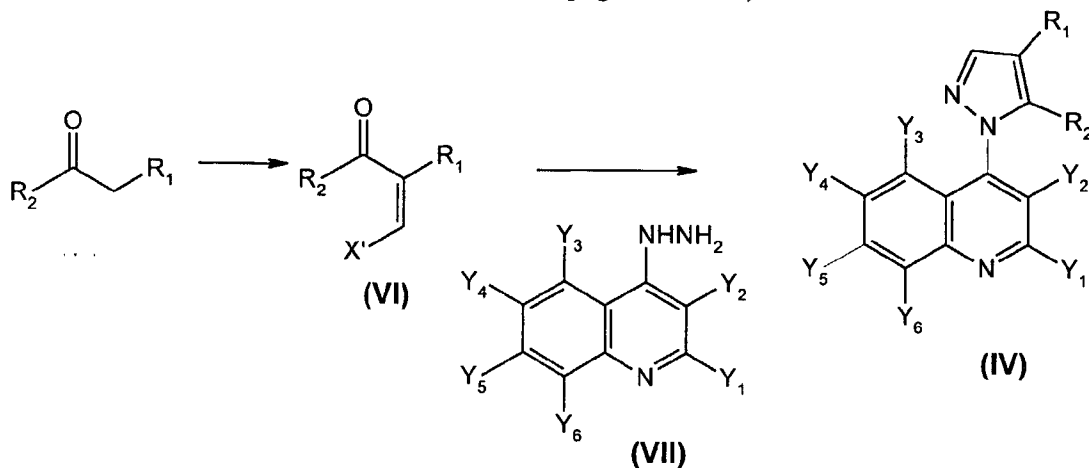
(1955).

[0020] Les composés de formule (IV) :



- 5 cas particulier des composés de formule (I) pour lesquels R_3 représente l'hydrogène et R_1 et R_2 sont respectivement en position 4 et 5 du noyau pyrazole, R_2 , Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 étant tels que définis précédemment, et R_1 représente un groupe carboxy, carbamoyle, N-alkylcarbamoyle, N,N-dialkylcarbamoyle, N-alkyl,N-alkoxyalkylcarbamoyle, N-alkoxycarbamoyle, N-alkyl-N-aminoalkylcarbamoyle, N,N-diaminoalkylcarbamoyle, alkoxy-carbonyl
- 10 inférieur; un nitrile, un groupe acyle inférieur,

peuvent avantageusement être préparés selon la réaction suivante (cf. Houben-Weyl, band E8b, Hetarene III, Teil 2 pages 450-472) :



15

où X' représente un atome d'halogène, N,N-dialkylamino ou alkoxy, R_1 , R_2 et Y_1 à Y_6 étant tels que définis pour les composés de formule (IV) ci-dessus.

- [0021] Les composés de formule (VII) peuvent avantageusement être préparés à partir des composés de formule (II) définis précédemment par réaction avec de
- 20 l'hydrazine selon des techniques classiques connues de l'homme du métier.

[0022] Une fois la construction du pyrazole achevée on peut faire des transformations classiques sur les groupements fonctionnels des substituants comme décrits dans de nombreux ouvrages généraux de chimie comme "Advanced Organic
5 Chemistry" de J. March, Ed. Wiley (1992), "Methoden der organischen Chemie" (Houben-Weyl), Ed. Georg Thieme Verlag ou les "Chemical Abstracts" Ed. American Chemical Society ainsi que dans les bases de données informatiques accessibles au public ou de manière plus précise sur des pyrazoles comme décrit dans Houben-Weyl, band E8b, Hetarene III, Teil 2 pages 580-656.

10

[0023] L'invention concerne également des compositions fongicides comportant une quantité efficace d'au moins une matière active de formule (I).

Les compositions fongicides selon l'invention comprennent un composé de formule (I) ou de formule (IV) ou un de ses sels acceptables en agriculture ou un
15 complexe métallique ou métalloïdique de ce composé, en association avec un support solide ou liquide, acceptable en agriculture et/ou un agent tensioactif également acceptable en agriculture. En particulier sont utilisables les supports inertes et usuels et les agents tensioactifs usuels. Ces compositions recouvrent non seulement les compositions prêtes à être appliquées sur la plante ou semence à traiter au moyen
20 d'un dispositif adapté, tel qu'un dispositif de pulvérisation ou de poudrage, mais également les compositions concentrées commerciales qui doivent être diluées avant application sur la culture.

[0024] Ces compositions fongicides selon l'invention peuvent contenir aussi toute
25 sorte d'autres ingrédients tels que, par exemple, des colloïdes protecteurs, des adhésifs, des épaississants, des agents thixotropes, des agents de pénétration, des stabilisants, des séquestrants, etc. Plus généralement, les matières actives peuvent être combinées à tous les additifs solides ou liquides correspondant aux techniques habituelles de la mise en formulation.

30

[0025] D'une façon générale, les compositions selon l'invention contiennent habituellement de 0,05 à 95 % (en poids) de matière active, un ou plusieurs supports solides ou liquides et, éventuellement, un ou plusieurs agents tensioactifs.

Par le terme "support", dans le présent exposé, on désigne une matière
35 organique ou minérale, naturelle ou synthétique, avec laquelle la matière active est combinée pour faciliter son application sur les parties de la plante. Ce support est donc généralement inerte et il doit être acceptable en agriculture. Le support peut être

solide (argiles, silicates naturels ou synthétiques, silice, résines, cires, engrais solides, etc.) ou liquide (eau, alcools, notamment le butanol etc...).

L'agent tensioactif peut être un agent émulsionnant, dispersant ou mouillant de type ionique ou non ionique ou un mélange de tels agents tensioactifs. On peut
5 citer par exemple des sels d'acides polyacryliques, des sels d'acides lignosulfoniques, des sels d'acides phénolsulfoniques ou naphthalènesulfoniques, des polycondensats d'oxyde d'éthylène sur des alcools gras ou sur des acides gras ou sur des amines grasses, des phénols substitués (notamment des alkylphénols ou des arylphénols), des
10 sels d'esters d'acides sulfosucciniques, des dérivés de la taurine (notamment des alkyltaurates), des esters phosphoriques d'alcools ou de phénols polyoxyéthylés, des esters d'acides gras et de polyols, les dérivés à fonction sulfates, sulfonates et phosphates des composés précédents. La présence d'au moins un agent tensioactif est généralement indispensable lorsque la matière active et/ou le support inerte ne sont pas solubles dans l'eau et que l'agent vecteur de l'application est l'eau.

15

[0026] Ainsi donc, les compositions à usage agricole selon l'invention peuvent contenir la matière active dans de très larges limites, allant de 0,05 % à 95 % (en poids). Leur teneur en agent tensioactif est avantageusement comprise entre 5 % et 40 % en poids. Sauf indication contraire les pourcentages donnés dans cette
20 description sont des pourcentages pondéraux.

[0027] Ces compositions selon l'invention sont elles-mêmes sous des formes assez diverses, solides ou liquides.

Comme formes de compositions solides, on peut citer les poudres pour
25 poudrage (à teneur en matière active pouvant aller jusqu'à 100 %) et les granulés, notamment ceux obtenus par extrusion, par compactage, par imprégnation d'un support granulé, par granulation à partir d'une poudre (la teneur en matière active dans ces granulés étant entre 0,5 et 80 % pour ces derniers cas).

30 [0028] Les compositions fongicides selon l'invention peuvent encore être utilisées sous forme de poudres pour poudrage ; on peut aussi utiliser des compositions comprenant 50 g de matière active et 950 g de talc ; on peut aussi utiliser des compositions comprenant 20 g de matière active, 10 g de silice finement divisée et 970 g de talc ; on mélange et broie ces constituants et on applique le mélange par
35 poudrage.

[0029] Comme formes de compositions liquides ou destinées à constituer des

compositions liquides lors de l'application, on peut citer les solutions, en particulier les concentrés solubles dans l'eau, les émulsions, les suspensions concentrées, les poudres mouillables (ou poudre à pulvériser).

- 5 [0030] Les suspensions concentrées, applicables en pulvérisation, sont préparées de manière à obtenir un produit fluide stable ne se déposant pas et elles contiennent habituellement de 10 à 75 % de matière active, de 0,5 à 15 % d'agents tensioactifs, de 0,1 à 10 % d'agents thixotropes, de 0 à 10 % d'additifs appropriés, comme des anti-mousses, des inhibiteurs de corrosion, des stabilisants, des agents de pénétration et
10 des adhésifs et, comme support, de l'eau ou un liquide organique dans lequel la matière active est peu ou pas soluble : certaines matières solides organiques ou des sels minéraux peuvent être dissous dans le support pour aider à empêcher la sédimentation ou comme antigels pour l'eau.

- 15 [0031] A titre d'exemple, voici une composition de suspension concentrée :

Exemple SC 1 :

| | | |
|----|---|---------|
| | - matière active | 500 g |
| | - phosphate de tristyrylphénol polyéthoxylé | 50 g |
| 20 | - alkylphénol polyéthoxylé | 50 g |
| | - polycarboxylate de sodium | 20 g |
| | - éthylène glycol | 50 g |
| | - huile organopolysiloxanique (antimousse) | 1 g |
| | - polysaccharide | 1,5 g |
| 25 | - eau | 316,5 g |

- [0032] Les poudres mouillables (ou poudre à pulvériser) sont habituellement préparées de manière qu'elles contiennent 20 à 95 % de matière active, et elles contiennent habituellement, en plus du support solide, de 0 à 30 % d'un agent mouillant, de 3 à 20 % d'un agent dispersant, et, quand c'est nécessaire, de 0,1 à 10 %
30 d'un ou plusieurs stabilisants et/ou autres additifs, comme des agents de pénétration, des adhésifs, ou des agents antimottants, colorants, etc...

- Pour obtenir les poudres à pulvériser ou poudres mouillables, on mélange intimement les matières actives dans les mélangeurs appropriés avec les substances
35 additionnelles et on broie avec des moulins ou autres broyeurs appropriés. On obtient par là des poudres à pulvériser dont la mouillabilité et la mise en suspension sont avantageuses ; on peut les mettre en suspension avec de l'eau à toute concentration

désirée et ces suspensions sont utilisables très avantageusement en particulier pour l'application par exemple sur les feuilles des végétaux ou sur les semences.

5 [0033] A titre d'exemple, voici diverses compositions de poudres mouillables (ou poudres à pulvériser) :

Exemple PM 1

| | | |
|----|---|-------|
| | - matière active | 50% |
| | - alcool gras éthoxylé (agent mouillant) | 2,5% |
| 10 | - phényléthylphénol éthoxylé (agent dispersant) | 5% |
| | - craie (support inerte) | 42,5% |

Exemple PM 2 :

| | | |
|----|---|--------------|
| | - matière active | 10% |
| 15 | - alcool synthétique oxo de type ramifié, en C13 éthoxylé par 8 à 10 oxyde d'éthylène (agent mouillant) | 0,75% |
| | - lignosulfonate de calcium neutre (agent dispersant) | 12% |
| | - carbonate de calcium (charge inerte) | q.s.p. 100 % |

20 **Exemple PM 3 :**

Cette poudre mouillable contient les mêmes ingrédients que dans l'exemple précédent, dans les proportions ci-après :

| | | |
|----|--|-------------|
| | - matière active | 75% |
| | - agent mouillant | 1,50% |
| 25 | - agent dispersant | 8% |
| | - carbonate de calcium (charge inerte) | q.s.p. 100% |

Exemple PM 4 :

| | | |
|----|---|-----|
| | - matière active | 90% |
| 30 | - alcool gras éthoxylé (agent mouillant) | 4% |
| | - phényléthylphénol éthoxylé (agent dispersant) | 6% |

Exemple PM 5 :

| | | |
|----|---|-------|
| | - matière active | 50% |
| 35 | - mélange de tensio-actifs anioniques et non ioniques (agent mouillant) | 2,5% |
| | - lignosulfonate de sodium (agent dispersant) | 5% |
| | - argile kaolinique (support inerte) | 42,5% |

[0034] Les dispersions et émulsions aqueuses, par exemple les compositions obtenues en diluant à l'aide d'eau une poudre mouillable selon l'invention, sont comprises dans le cadre général de la présente invention. Les émulsions peuvent être
5 du type eau-dans-l'huile ou huile-dans-l'eau et elles peuvent avoir une consistance épaisse comme celle d'une "mayonnaise".

[0035] Les compositions fongicides selon l'invention peuvent être formulées sous la forme de granulés dispersables dans l'eau également compris dans le cadre de
10 l'invention.

Ces granulés dispersables, de densité apparente généralement comprise entre environ 0,3 et 0,6 ont une dimension de particules généralement comprise entre environ 150 et 2000 et de préférence entre 300 et 1500 microns.

[0036] La teneur en matière active de ces granulés est généralement comprise entre environ 1 % et 90 %, et de préférence entre 25 % et 90 %.

Le reste du granulé est essentiellement composé d'une charge solide et éventuellement d'adjuvants tensio-actifs conférant au granulé des propriétés de dispersibilité dans l'eau. Ces granulés peuvent être essentiellement de deux types
20 distincts selon que la charge retenue est soluble ou non dans l'eau. Lorsque la charge est hydrosoluble, elle peut être minérale ou, de préférence, organique. On a obtenu d'excellents résultats avec l'urée. Dans le cas d'une charge insoluble, celle-ci est de préférence minérale, comme par exemple le kaolin ou la bentonite. Elle est alors avantageusement accompagnée d'agents tensio-actifs (à raison de 2 à 20 % en poids
25 du granulé) dont plus de la moitié est, par exemple, constituée par au moins un agent dispersant, essentiellement anionique, tel qu'un polynaphtalène sulfonate alcalin ou alcalino terreux ou un lignosulfonate alcalin ou alcalino-terreux, le reste étant constitué par des mouillants non ioniques ou anioniques tel qu'un alcoyl naphtalène sulfonate alcalin ou alcalino-terreux. Par ailleurs, bien que cela ne soit pas
30 indispensable, on peut ajouter d'autres adjuvants tels que des agents anti-mousse.

[0037] Le granulé selon l'invention peut être préparé par mélange des ingrédients nécessaires puis granulation selon plusieurs techniques en soi connues (drageoir, lit fluide, atomiseur, extrusion, etc.). On termine généralement par un concassage suivi
35 d'un tamisage à la dimension de particule choisie dans les limites mentionnées ci-dessus. On peut encore utiliser des granulés obtenus comme précédemment puis imprégnés avec une composition contenant la matière active.

De préférence, il est obtenu par extrusion, en opérant comme indiqué dans les exemples ci-après.

Exemple GD1 : Granulés dispersables

5 Dans un mélangeur, on mélange 90 % en poids de matière active et 10 % d'urée en perles. Le mélange est ensuite broyé dans un broyeur à broches. On obtient une poudre que l'on humidifie avec environ 8 % en poids d'eau. La poudre humide est extrudée dans une extrudeuse à rouleau perforé. On obtient un granulé qui est séché, puis concassé et tamisé, de façon à ne garder respectivement que les granulés
10 d'une dimension comprise entre 150 et 2000 microns.

Exemple GD2 : Granulés dispersables

Dans un mélangeur, on mélange les constituants suivants :

| | | |
|----|---|-----|
| | - matière active | 75% |
| 15 | - agent mouillant (alkylnaphtalène sulfonate de sodium) | 2% |
| | - agent dispersant (polynaphtalène sulfonate de sodium) | 8% |
| | - charge inerte insoluble dans l'eau (kaolin) | 15% |

Ce mélange est granulé en lit fluide, en présence d'eau, puis séché, concassé et tamisé
20 de manière à obtenir des granulés de dimension comprise entre 0,15 et 0,80 mm.

[0038] Ces granulés peuvent être utilisés seuls, en solution ou dispersion dans de l'eau de manière à obtenir la dose cherchée. Ils peuvent aussi être utilisés pour préparer des associations avec d'autres matières actives, notamment fongicides, ces
25 dernières étant sous la forme de poudres mouillables, ou de granulés ou suspensions aqueuses.

[0039] Les composés de l'invention peuvent aussi être mélangés avec un ou plusieurs insecticides, fongicides, bactéricides, acaricides, arthropodicides,
30 nématocides, attractants ou phéromones ou autres composés à activité biologique. Les mélanges ainsi obtenus ont une activité à spectre élargi. Les mélanges avec d'autres fongicides sont particulièrement avantageux, par exemple les mélanges avec les fongicides de la famille des triazoles, des dérivés de la strobilurine etc. Les composés de la présente invention peuvent avantageusement être utilisés en
35 association avec l'azoxystrobine, le krésoxym-méthyl, la discostrobine, le carbendazim, le thiram, le diéthofencarb, la dodine, le manèbe, le mancozèbe, le diflumetorim, l'ethirimol, le bénomyl, le cymoxanil, la fenpropidine, le

fenpropimorph, le triadimefon, le captane, le captafol, le folpel, le thiophanate, le thiabendazole, l'acide phosphorique et ses dérivés comme le phosetyl-Al, le chlorothalonil, les compositions fongicides à base de cuivre, le dichloran, le metalaxyl, l'iprodione, la fénamidone, l'oxadixyl, la vinchlozoline, le tébuconazole, le
5 bromuconazole, le triticonazole, le difenconazole, le diniconazole, le metconazole, le penconazole, le propiconazole, le prochloraz, le fénarimol, le triadiménol, le furalaxyl, les dérivés du cuivre comme l'hydroxyde et l'oxychlorure, le probénazole, l'époxyconazole, la famoxadone, la picoxystrobine, le fludioxonyl, le pyriméthanil, le mépanipyrin, le cyprodinyl, le quinoxyfen, la ferimzone, le fluazinam, la
10 trifloxystrobine, le diméthomorphe, le béalaxyl, la blasticidin-S, le fluquinconazole, le tricyclazole, le fluzilazole, les dérivés de la valinamide, comme par exemple l'iprovalicarb, le flutolanil, la guazatine, l'hexaconazole, l'hymexazol, l'isoprothiolane, la kazugamycine, le pencycuron, le phtalide, le pyroquilon, le tétraconazole, le thifluzamide et la carboxine.

15

[0040] Les compositions selon l'invention sont également utiles pour traiter les semences, par exemple de céréales (blé, seigle, triticales et orge notamment), de pomme de terre, de coton, de pois, de colza, de maïs, de lin ou encore les semences d'arbres forestiers (notamment de résineux). On notera à ce propos que dans le jargon
20 de l'homme de métier, le terme traitement de semences se rapporte en fait au traitement des graines. Les techniques d'application sont bien connues de l'homme de métier et elles peuvent être utilisées sans inconvénient dans le cadre de la présente invention. On pourra citer par exemple le pelliculage ou l'enrobage.

25 [0041] Il a été découvert de façon tout à fait surprenante que les composés de formule (I) selon l'invention sont des composés fongicides actifs sur une très large gamme de champignons phytopathogènes des cultures. Cette activité s'est révélée lors de traitements préventifs, mais aussi lors de traitements curatifs. De plus, cette activité s'est montrée très intéressante même en employant des faibles doses de
30 composés de formule (I).

[0042] De façon tout à fait surprenante pour des composés possédant une telle activité (large spectre d'action et faibles doses employées), ces composés de formule (I) ne sont pas ou très faiblement phytotoxiques. C'est-à-dire qu'ils possèdent une très
35 bonne sélectivité vis-à-vis des plantes traitées.

Enfin, les composés de formule (I) ont un comportement très favorable au regard de l'environnement en ce sens qu'ils ne sont pas ou très faiblement écotoxiques.

[0043] Ainsi, l'invention a pour autre objet un procédé de lutte, à titre curatif ou préventif, contre les champignons phytopathogènes des cultures, caractérisé en ce que les semences, les feuilles ou les troncs de végétaux ou les sols où poussent ou
5 sont susceptibles de pousser ces végétaux sont traités par application, pulvérisation ou injection d'une quantité efficace (agronomiquement efficace) et non phytotoxique d'une matière active de formule (I) ou un de ses sels acceptables en agriculture ou un complexe métallique ou métalloïdique de ce composé également acceptable en agriculture, de préférence sous forme d'une composition fongicide selon l'invention.

10

[0044] Par "quantité efficace et non phytotoxique", on entend une quantité de composition selon l'invention suffisante pour permettre le contrôle ou la destruction des champignons présents ou susceptibles d'apparaître sur les cultures, et n'entraînant pour lesdites cultures aucun symptôme notable de phytotoxicité. Une telle quantité
15 est susceptible de varier dans de larges limites selon le champignon à combattre, le type de culture, les conditions climatiques, et les composés compris dans la composition fongicide selon l'invention. Cette quantité peut être déterminée par des essais systématiques au champ, à la portée de l'homme du métier.

20 [0045] La dose de composition appliquée est, en général, de façon avantageuse telle que la dose de matière active est comprise entre 2 et 200 g de matière active par 100 kg de semence, de préférence entre 3 et 150 g par 100 kg dans le cas des traitements de semences.

Dans le cas des traitements de végétaux, des doses de 10 à 800 g/ha, de
25 préférence 50 à 300 g/ha sont généralement appliqués en traitement foliaire. Il doit être compris que ces doses sont données à titre purement illustratifs pour les besoins de la présente invention.

Ainsi, l'homme du métier sera à même d'évaluer les doses précises de matières actives à appliquer, selon la nature et le degré de développement des
30 cultures, selon la nature des maladies à éradiquer et leur stade d'infestation, ainsi que des conditions édaphiques et climatiques présentes sur le terrain au moment ou avant ou après le ou les traitements.

[0046] De même, le nombre et la fréquence des traitements pourra varier en
35 fonction des mêmes critères évoqués précédemment. Ainsi l'homme du métier jugera bon d'effectuer un ou plusieurs traitements de manière préventive, c'est-à-dire avant l'apparition des maladies, associés ou non à un ou plusieurs traitements curatifs,

destinés à éradiquer les maladies déjà apparues.

[0047] L'invention concerne enfin une méthode de protection à titre préventif ou curatif des produits de multiplication des végétaux, ainsi que des végétaux en
5 résultant, contre les maladies fongiques, caractérisée en ce que l'on recouvre lesdits produits d'une dose efficace et non phytotoxique d'une composition selon l'invention.

Parmi les produits de multiplications des végétaux concernés, on peut citer notamment les semences ou graines, et les tubercules.

Comme cela a été indiqué précédemment, les modalités de recouvrement
10 des produits de multiplication des végétaux, notamment des semences, sont bien connues dans l'art et font appel en particulier aux techniques de pelliculage ou d'enrobage.

[0048] Les produits et compositions selon l'invention peuvent aussi s'appliquer en
15 application foliaire sur les cultures végétales.

Parmi les végétaux visés par la méthode selon l'invention, on peut citer à titre d'exemples non limitatifs :

- le blé, en ce qui concerne la lutte contre les maladies suivantes des semences : les fusarioses (*Microdochium nivale* et *Fusarium roseum*), les caries (*Tilletia caries*,
20 *Tilletia controversa* ou *Tilletia indica*), la septoriose (*Septoria nodorum*) ;

- le blé, en ce qui concerne la lutte contre les maladies suivantes des parties aériennes de la plante : le piétin-verse (*Pseudocercospora herpotrichoides*), le piétin-échaudage (*Gaeumannomyces graminis*), la fusariose du pied (*F. culmorum*, *F. graminearum*), la fusariose des épis (*F. culmorum*, *F. graminearum*, *Microdochium*
25 *nivale*), l'helminthosporiose (*Pyrenophora tritici-repentis*) le rhizoctone (*Rhizoctonia cerealis*), l'oïdium (*Erysiphe graminis forma specie tritici*), les rouilles (*Puccinia striiformis* et *Puccinia recondita*) et les septorioses (*Septoria tritici* et *Septoria nodorum*) ;

- le blé et l'orge, en ce qui concerne la lutte contre les maladies bactériennes et
30 virales, par exemple la jaunisse nanisante de l'orge.

- l'orge, en ce qui concerne la lutte contre les maladies suivantes des semences : les helminthosporioses (*Pyrenophora graminea*, *Pyrenophora teres* et *Cochliobolus sativus*), le charbon nu (*Ustilago nuda*) et les fusarioses (*Microdochium nivale* et *Fusarium roseum*),

- l'orge, en ce qui concerne la lutte contre les maladies suivantes des parties
35 aériennes de la plante : le piétin-verse (*Pseudocercospora herpotrichoides*), les helminthosporioses (*Pyrenophora teres* et *Cochliobolus sativus*), l'oïdium (*Erysiphe*

graminis forma specie hordei), la rouille naine (*Puccinia hordei*) et la rhynchosporiose (*Rhynchosporium secalis*) ;

- la pomme de terre, en ce qui concerne la lutte contre les maladies du tubercule (notamment *Helminthosporium solani*, *Phoma tuberosa*, *Rhizoctonia solani*,
5 *Fusarium solani*), le mildiou (*Phytophthora infestans*) et certaines viroses (virus Y) ;

- la pomme de terre en ce qui concerne la lutte contre les maladies du feuillage suivantes : l'alternariose (*Alternaria solani*), le mildiou (*Phytophthora infestans*) ;

- le coton, en ce qui concerne la lutte contre les maladies suivantes des jeunes plantes issues des semences : les fontes de semis et les nécroses du collet
10 (*Rhizoctonia solani*, *Fusarium oxysporum*), la pourriture noire des racines (*Thielaviopsis basicola*) ;

- les cultures protéagineuses, par exemple le pois, en ce qui concerne la lutte contre les maladies suivantes des semences : l'anthracnose (*Ascochyta pisi*,
15 *Mycosphaerella pinodes*), la fusariose (*Fusarium oxysporum*), la pourriture grise (*Botrytis cinerea*), le mildiou (*Peronospora pisi*) ;

- les cultures oléagineuses, par exemple le colza, en ce qui concerne la lutte contre les maladies suivantes des semences : *Phoma lingam*, *Alternaria brassicae* ;
Sclerotinia sclerotiorum,

- le maïs, en ce qui concerne la lutte contre les maladies des semences : (*Rhizopus*
20 *sp.*, *Penicillium sp.*, *Trichoderma sp.*, *Aspergillus sp.* et *Gibberella fujikuroi*) ;

- le lin, en ce qui concerne la lutte contre la maladie des semences : *Alternaria linicola* ;

- les arbres forestiers, en ce qui concerne la lutte contre les fontes de semis (*Fusarium oxysporum*, *Rhizoctonia solani*).

25 - les cultures légumières en ce qui concerne la lutte contre les maladies suivantes des semis ou des jeunes plants issus de semences : les fontes de semis et les nécroses du collet (*Fusarium oxysporum*, *Fusarium roseum*, *Rhizoctonia solani*, *Pythium sp.*)

- les cultures légumières en ce qui concerne la lutte contre les maladies
30 suivantes des parties aériennes : la pourriture grise (*Botrytis sp.*), les oïdiums (notamment *Erysiphe cichoracearum*, *Sphaerotheca fuliginea*, *Leveillula taurica*), les fusarioses (*Fusarium oxysporum*, *Fusarium roseum*), les cladosporioses (*Cladosporium sp.*), les alternarioses (*Alternaria sp.*), les anthracnoses (*Colletotrichum sp.*), les septorioses (*Septoria sp.*), le rhizoctone (*Rhizoctonia solani*), les mildious (par exemple *Bremia lactucae*, *Peronospora sp.*,
35 *Pseudoperonospora sp.*, *Phytophthora sp.*).

- les arbres fruitiers en ce qui concerne les maladies des parties aériennes : la

moniliose (*Monilia fructigena*), la tavelure (*Venturia inaequalis*), l'oïdium (*Sphaerotheca fructigena*)

- la vigne en ce qui concerne les maladies du feuillage : notamment la pourriture grise (*Botrytis cinerea*), l'oïdium (*Uncinula necator*), le black-rot
5 (*Guignardia biwelli*), le mildiou (*Plasmopara viticola*)

- la betterave en ce qui concerne les maladies suivantes des parties aériennes : la cercosporiose (*Cercospora beticola*), l'oïdium (*Erysiphe beticola*), la ramulariose (*Ramularia beticola*)

Le blé et l'orge sont les végétaux préférés pour la mise en oeuvre de la
10 méthode selon l'invention.

[0049] La présente invention concerne également le traitement des plantes génétiquement modifiées avec les composés selon l'invention ou les compositions agrochimiques selon l'invention. Les plantes génétiquement modifiées sont des
15 plantes dans le génome desquelles un gène hétérologue codant pour une protéine d'intérêt a été intégré de manière stable.

[0050] Par gène hétérologue codant pour une protéine d'intérêt on entend
20 essentiellement selon l'invention les gènes conférant à la plante transformée de nouvelles propriétés agronomiques, ou les gènes d'amélioration de la qualité agronomique de la plante transformée.

[0051] Parmi les gènes conférant de nouvelles propriétés agronomiques aux plantes transformées, on peut citer les gènes conférant une tolérance à certains herbicides,
25 ceux conférant une résistance à certains insectes, ceux conférant une tolérance à certaines maladies, etc. De tels gènes sont notamment décrits dans les demandes de brevet WO 91/02071 et WO 95/06128.

[0052] Parmi les gènes conférant une tolérance à certains herbicides, on peut citer
30 le gène *Bar* conférant une tolérance au bialaphos, le gène codant pour une EPSPS appropriée conférant une résistance aux herbicides ayant l'EPSPS comme cible comme le glyphosate et ses sels (US 4,535,060, US 4,769,061, US 5,094,945, US 4,940,835, US 5,188,642, US 4,971,908, US 5,145,783, US 5,310,667, US
35 5,312,910, US 5,627,061, US 5,633,435, FR 2 736 926), le gène codant pour la glyphosate oxydoréductase (US 5,463,175), ou encore un gène codant pour une HPPD conférant une tolérance aux herbicides ayant pour cible l'HPPD comme les

isoxazoles, notamment l'isoxafutole (FR 95 06800, FR 95 13570), les dicétonitriles (EP 496 630, EP 496 631) ou les tricétones, notamment la sulcotrione (EP 625 505, EP 625 508, US 5,506,195). De tels gènes codant pour une HPPD conférant une tolérance aux herbicides ayant pour cible l'HPPD sont décrits dans la demande de
5 brevet WO 96/38567.

Dans les cas des gènes codant pour EPSPS ou HPPD, et plus particulièrement pour les gènes ci-dessus, la séquence codant pour ces enzymes est avantageusement précédée par une séquence codant pour un peptide de transit, en particulier pour le peptide de transit dit peptide de transit optimisé décrit dans les
10 brevets US 5,510,471 ou US 5,633,448.

[0053] Parmi les gènes conférant de nouvelles propriétés de résistance aux insectes, on citera plus particulièrement les gènes codant pour les protéines *Bt* largement décrites dans la littérature et bien connues de l'homme du métier. On citera aussi les
15 gènes codant pour les protéines extraites de bactéries comme *Photobacterium* (WO 97/17432 & WO 98/08932).

[0054] Parmi les gènes conférant de nouvelles propriétés de résistance aux maladies
20 on citera notamment les gènes codant pour les chitinases, les glucanases, l'oxalate oxydase, toutes ces protéines et leurs séquences codantes étant largement décrites dans la littérature, ou encore les gènes codant pour des peptides antibactériens et/ou antifongiques, en particulier des peptides de moins de 100 acides aminés riches en cystéines comme les thionines ou défensines de plantes, et plus particulièrement les
25 peptides lytiques de toutes origines comprenant un ou plusieurs ponts disulfures entre les cystéines et des régions comprenant des acides aminés basiques, notamment les peptides lytiques suivants : l'androctonine (WO 97/30082 et PCT/FR98/01814, déposée le 18 août 1998) ou la drosomicine (PCT/FR98/01462, déposée le 8 juillet 1998). On citera également les gènes codant pour des peptides éliciteurs fongiques,
30 en particulier les élicitines (Kamoun & al., 1993 ; Panabières & al., 1995).

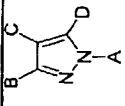
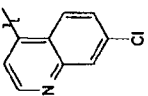

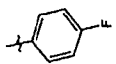
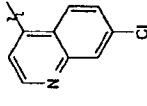

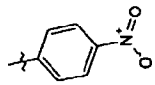
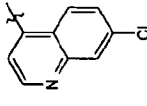


[0055] Parmi les gènes modifiant la constitution des plantes modifiées, on peut citer en particulier les gènes modifiant la teneur et la qualité de certains acides gras essentiels (EP 666 918) ou encore la teneur et la qualité des protéines, en particuliers
35 dans les feuilles et/ou les graines desdites plantes. On citera en particulier les gènes codant pour des protéines enrichies en acides aminés soufrés (Korit, A.A. & al., Eur. J. Biochem. (1991) 195, 329-334 ; WO 98/20133 ; WO 97/41239 ; WO 95/31554 ;

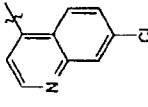

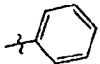
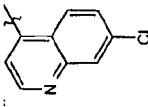


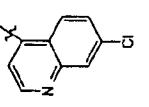


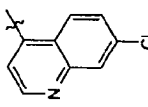

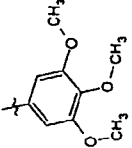
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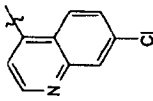

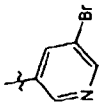
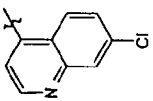

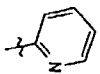
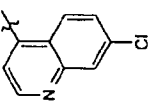

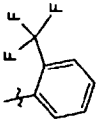
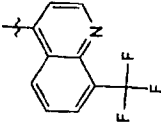


[0056] La présente invention concerne plus particulièrement le traitement des plantes génétiquement modifiées comprenant un gène hétérologue conférant à la
5 plante des propriétés de résistance aux maladies. De manière préférentielle, le gène hétérologue confère à la plante génétiquement modifiée un spectre d'activité complémentaire du spectre d'activité des composés selon l'invention.

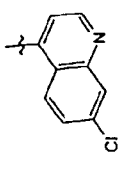

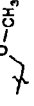
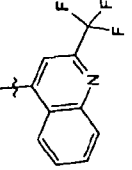

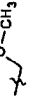
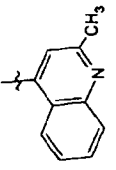


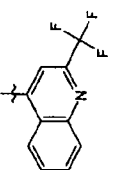


Par spectre complémentaire, on entend selon l'invention un spectre d'activité pour le gène hétérologue distinct du spectre d'activité des composés selon
10 l'invention, ou un spectre d'activité portant sur des agents infectieux identiques mais permettant un contrôle identique ou amélioré pour de moindres doses d'application en composés selon l'invention.

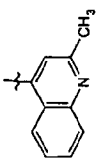

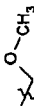
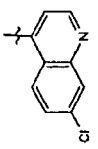

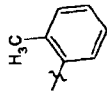
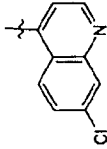


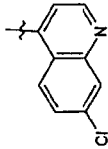


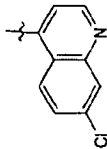

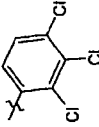
[0057] Le tableau suivant illustre de manière non limitative quelques exemples de
15 composés fongicides selon l'invention (les différents composés ont été analysés par spectrométrie de masse ; la colonne « Masse observée » fournit la masse + 1 ou la masse -1 du pic moléculaire observé) :

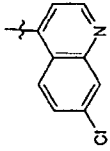

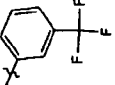
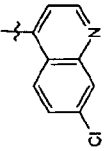


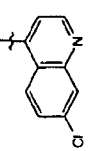

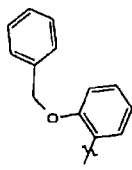
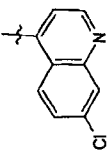

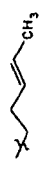
| | n° | A | B | C | D | Masse théorique | Masse observée |
|---|----|--|---|--|---|--------------------|-------------------|
| | |  | | | | | |
| 1 | |  | H |  |  | 381 | |
| 2 | |  | H |  |  | 408 | |
| 3 | |  | H |  |  | 301 | |

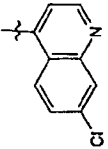

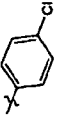
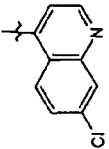

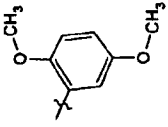
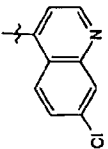

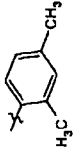
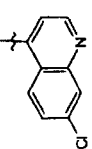

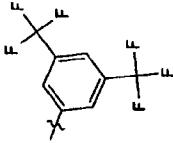
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 4 |  | H |  |  | 363 | |
| 5 |  | H |  |  | 329 | |
| 6 |  | H |  |  | 331 | 332 (M+1) |
| 7 |  | H |  |  | 453 | |

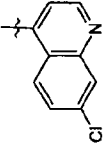


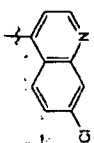

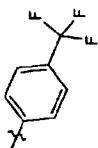
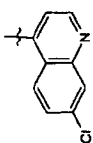

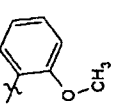
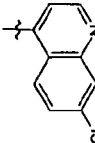

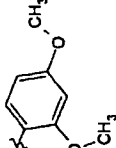
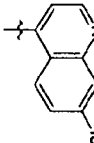

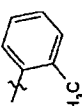
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|---|---|--------------------|-------------------|
| 8 |  | H |  |  | 442 | |
| 9 |  | H |  |  | 364 | |
| 10 |  | H |  |  | 431 | |
| 11 |  |  |  | H | 365 | 366 (M+1) |

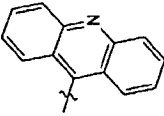


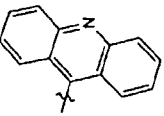

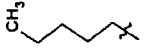
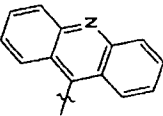


| n° | A | B | C | D | Masse théorique | Masse observée |
|----|--|---|--|---|--------------------|-------------------|
| 12 |  | H |  |  | 317 | |
| 13 |  | H |  |  | 351 | |
| 14 |  | H |  |  | 297 | |
| 15 |  | H |  |  | 365 | |

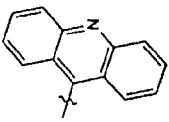

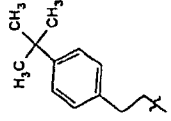
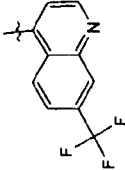


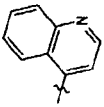


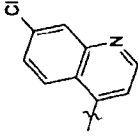


| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 16 |  | H |  |  | 311 | |
| 17 |  | H |  |  | 377 | |
| 18 |  | H |  |  | 381 | |
| 19 |  | H |  |  | 315 | |
| 20 |  | H |  |  | 465 | |

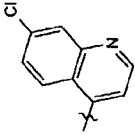

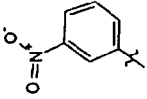
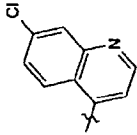

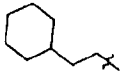
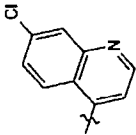

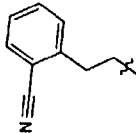
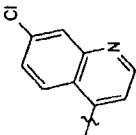

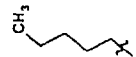
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|--|---|--|---|--------------------|-------------------|
| 21 |  | H |  |  | 431 | |
| 22 |  | H |  |  | 397 | |
| 23 |  | H |  |  | 469 | |
| 24 |  | H |  |  | 355 | |

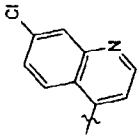

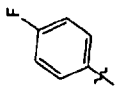
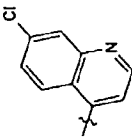

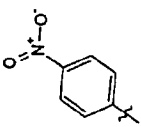
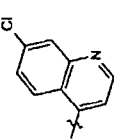


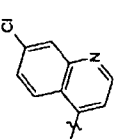


| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|--|--------------------|-------------------|
| 25 |  | H |  |  | 397 | |
| 26 |  | H |  |  | 423 | |
| 27 |  | H |  |  | 391 | |
| 28 |  | H |  |  | 499 | |

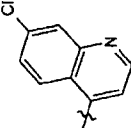

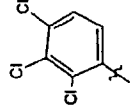
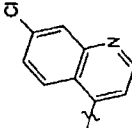

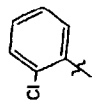
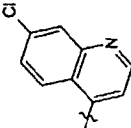


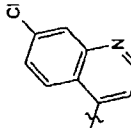

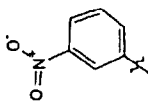
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 29 |  | H |  |  | 329 | |
| 30 |  | H |  |  | 431 | |
| 31 |  | H |  |  | 393 | |
| 32 |  | H |  |  | 423 | |
| 33 |  | H |  |  | 363 | |

| n° | A | B | C | D | Masse théorique | Masse observée |
|----|--|---|---|--|--------------------|-------------------|
| 34 |  | H |  |  | 331 | |
| 35 |  | H |  |  | 373 | |
| 36 |  | H |  |  | 399 | |

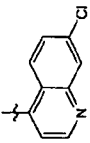
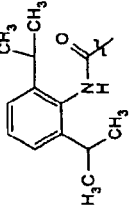
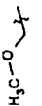
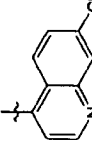
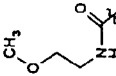
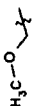
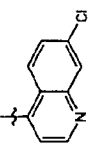
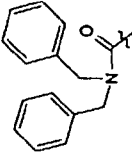

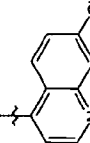
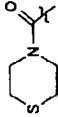
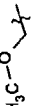
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|---|---|--------------------|-------------------|
| 37 |  | H |  |  | 463 | |
| 38 |  | H |  |  | 365 | 366 (M+1) |
| 39 |  | H |  |  | 297 | |
| 40 |  | H |  |  | 364 | |

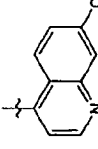
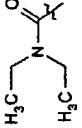
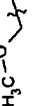
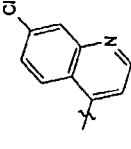


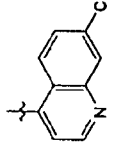

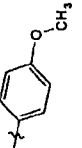
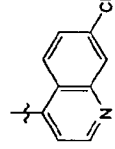

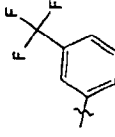
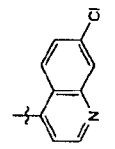

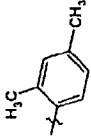
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|---|---|--------------------|-------------------|
| 41 |  | H |  |  | 408 | |
| 42 |  | H |  |  | 397 | |
| 43 |  | H |  |  | 416 | |
| 44 |  | H |  |  | 357 | |

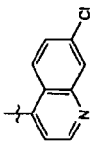

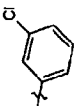
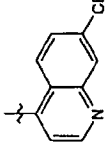
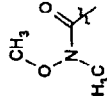
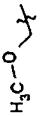
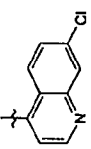


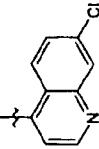
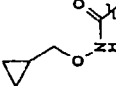
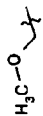
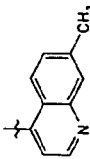

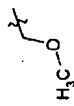
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 45 |  | H |  |  | 367 | 368 (M+1) |
| 46 |  | H |  |  | 394 | 393 (M-1) |
| 47 |  | H |  |  | 367 | 368 (M+1) |
| 48 |  | H |  |  | 301 | 300 (M-1) |

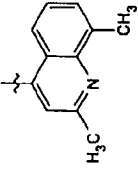


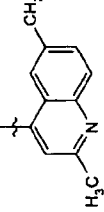


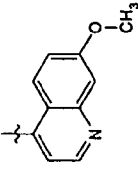


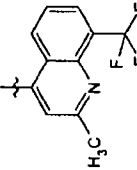


| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 49 |  | H |  |  | 451 | 452 (M+1) |
| 50 |  | H |  |  | 383 | 384 (M+1) |
| 51 |  | H |  |  | 315 | 316 (M+1) |
| 52 |  | H |  |  | 394 | 395 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|---|---|--------------------|-------------------|
| 53 | | H | | | 383 | 384 (M+1) |
| 54 | | H | | | 353 | |
| 55 | | H | | | 436 | |
| 56 | | H | | | 451 | |

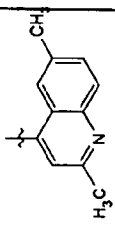
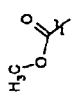
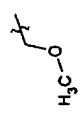
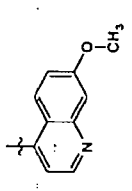
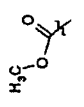
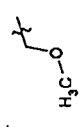
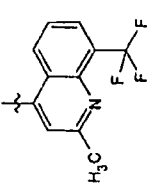
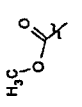
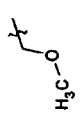
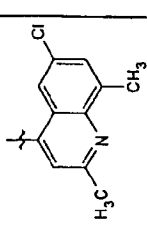
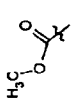
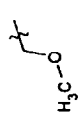
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 57 |  | H |  |  | 476 | |
| 58 |  | H |  |  | 374 | |
| 59 |  | H |  |  | 496 | |
| 60 |  | H |  |  | 402 | |

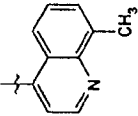

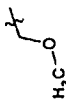
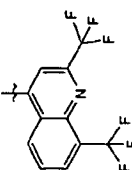

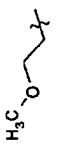
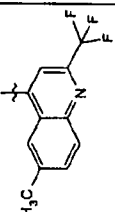

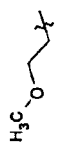
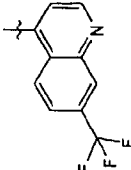

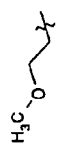
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|---|---|--------------------|-------------------|
| 61 |  | H |  |  | 372 | 373 (M+1) |
| 62 |  | H |  |  | 349 | 350 (M+1) |
| 63 |  | H |  |  | 379 | 380 (M+1) |
| 64 |  | H |  |  | 417 | 418 (M+1) |
| 65 |  | H |  |  | 377 | 376 (M-1) |

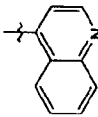
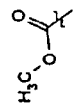
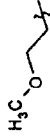
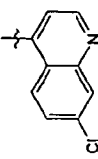
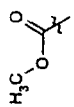
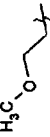
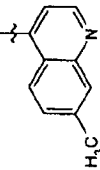
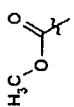

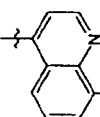
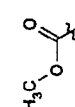

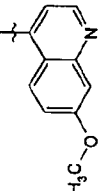
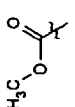
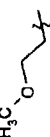
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 66 |  | H |  |  | 383 | 384 (M+1) |
| 67 |  | H |  |  | 360 | 361 (M+1) |
| 68 |  | H |  |  | 346 | 347 (M+1) |
| 69 |  | H |  |  | 386 | 387 (M+1) |
| 70 |  | H |  |  | 297 | |

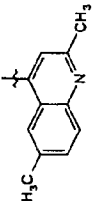

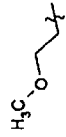
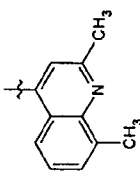

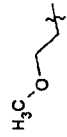
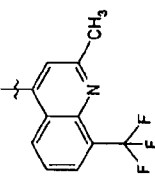


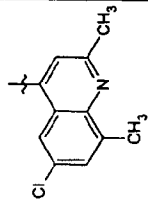


| n° | A | B | C | D | Masse théorique | Masse observée |
|----|--|---|---|---|--------------------|-------------------|
| 71 |  | H |  |  | 311 | |
| 72 |  | H |  |  | 311 | |
| 73 |  | H |  |  | 313 | |
| 74 |  | H |  |  | 365 | |

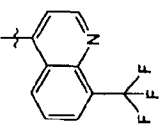


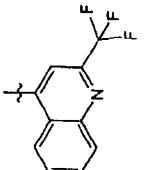


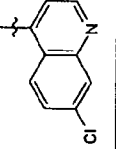


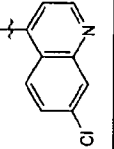

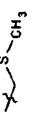
| n' | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|---|---|--------------------|-------------------|
| 75 | | H | | | 345 | |
| 76 | | H | | | 297 | |
| 77 | | H | | | 311 | |
| 78 | | H | | | 325 | |

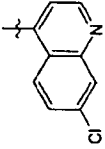
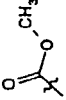

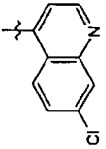
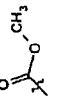
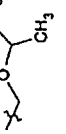
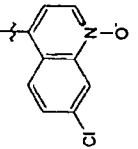
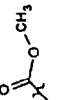
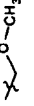
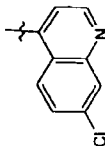
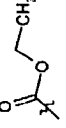

| n° | A | B | C | D | Masse théorique | Masse observée |
|----|--|---|--|---|--------------------|-------------------|
| 79 |  | H |  |  | 325 | |
| 80 |  | H |  |  | 327 | |
| 81 |  | H |  |  | 379 | |
| 82 |  | H |  |  | 359 | |

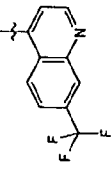

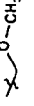
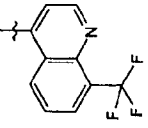

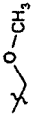
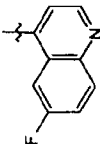

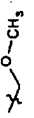
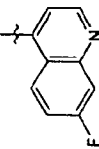

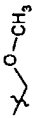
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 83 |  | H |  |  | 311 | |
| 84 |  | H |  |  | 447 | 448 (M+1) |
| 85 |  | H |  |  | 393 | 394 (M+1) |
| 86 |  | H |  |  | 379 | 380 (M+1) |

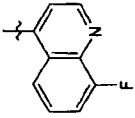

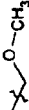
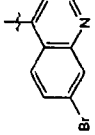

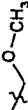
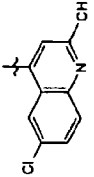


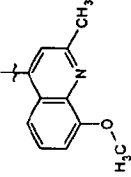

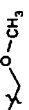
| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 87 |  | H |  |  | 311 | 312 (M+1) |
| 88 |  | H |  |  | 345 | |
| 89 |  | H |  |  | 325 | |
| 90 |  | H |  |  | 325 | |
| 91 |  | H |  |  | 341 | |

| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 92 |  | H |  |  | 339 | |
| 93 |  | H |  |  | 339 | |
| 94 |  | H |  |  | 393 | |
| 95 |  | H |  |  | 373 | |

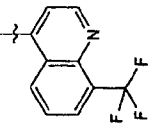

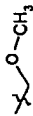
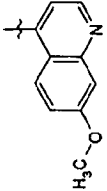

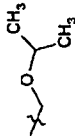
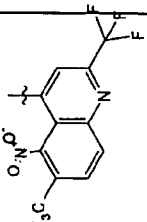


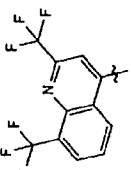


| n° | A | B | C | D | Masse théorique | Masse observée |
|----|---|---|--|---|--------------------|-------------------|
| 96 |  | H |  |  | 379 | 380 (M+1) |
| 97 |  | H |  |  | 379 | 380 (M+1) |
| 98 |  |  |  | H | 269 | |
| 99 |  | H |  |  | 347 | |

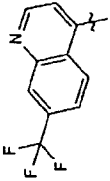
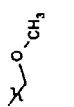
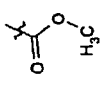
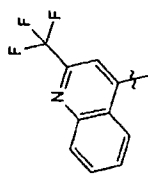
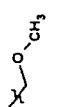
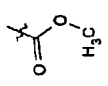
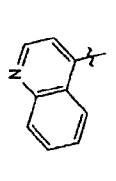
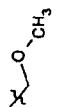
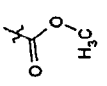
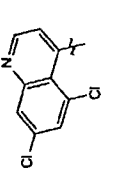
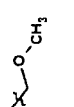
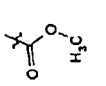
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 100 |  | H |  |  | 379 | 380 (M+1) |
| 101 |  | H |  |  | 359 | 360 (M+1) |
| 102 |  | H |  |  | 347 | |
| 103 |  | H |  |  | 345 | 346 (M+1) |

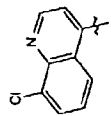
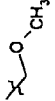

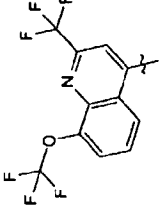
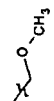

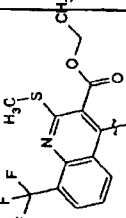
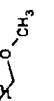

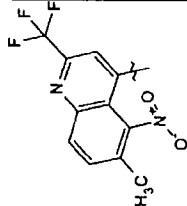
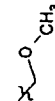

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 104 |  | H |  |  | 351 | |
| 105 |  | H |  |  | 351 | |
| 106 |  | H |  |  | 301 | |
| 107 |  | H |  |  | 301 | |

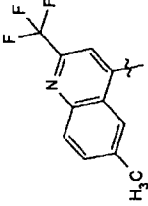
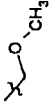

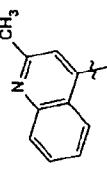
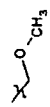

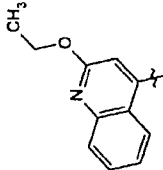
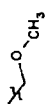

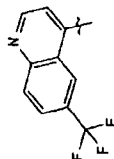
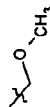

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 108 |  | H |  |  | 301 | |
| 109 |  | H |  |  | 361 | |
| 110 |  | H |  |  | 331 | |
| 111 |  | H |  |  | 327 | |

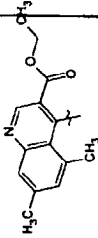
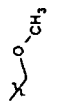

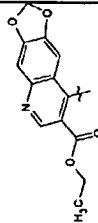
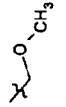

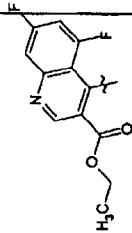
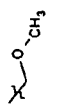

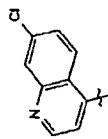
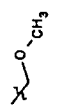

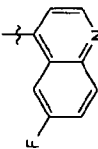

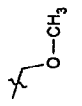
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 112 | | H | | | 331 | |
| 113 | | H | | | 325 | |
| 114 | | H | | | 361 | |
| 115 | | | H | | 315 | |

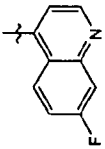


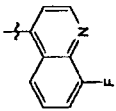


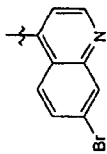


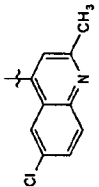


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 116 |  | H |  |  | 365 | |
| 117 |  | H |  |  | 355 | 356 (M+1) |
| 118 |  | H |  |  | 438 | 439 (M+1) |
| 119 |  |  |  | H | 433 | 434 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|--|---|---|--------------------|-------------------|
| 120 |  |  |  | H | 365 | 366 (M+1) |
| 121 |  |  |  | H | 365 | 366 (M+1) |
| 122 |  |  |  | H | 297 | 298 (M+1) |
| 123 |  |  |  | H | 365 | 366 (M+1) |

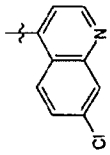
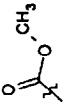
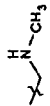
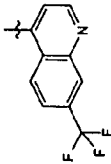
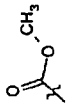

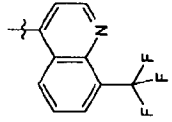
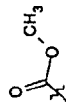

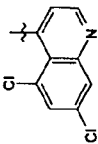
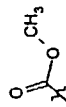

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 124 |  |  |  | H | 331 | 330 (M-1) |
| 125 |  |  |  | H | 449 | 450 (M+1) |
| 126 |  |  |  | H | 483 | 484 (M+1) |
| 127 |  |  |  | H | 424 | 425 (M+1) |

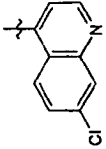

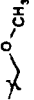
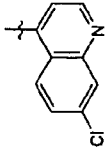


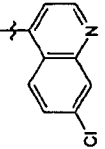
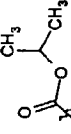

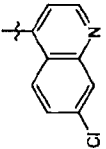
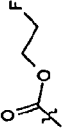
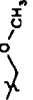
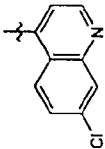
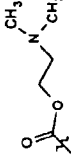
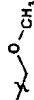
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 128 |  |  |  | H | 379 | 380 (M+1) |
| 129 |  |  |  | H | 311 | 312 (M+1) |
| 130 |  |  |  | H | 341 | 340 (M-1) |
| 131 |  |  |  | H | 365 | 366 (M+1) |

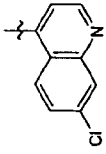


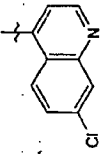

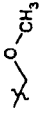
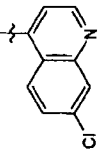

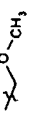
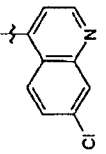

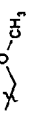
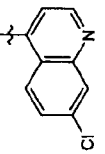

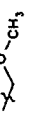
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|--|--|---|--------------------|-------------------|
| 132 |  |  |  | H | 397 | 398 (M+1) |
| 133 |  |  |  | H | 413 | 414 (M+1) |
| 134 |  |  |  | H | 405 | 406 (M+1) |
| 135 |  |  |  | H | 331 | |
| 136 |  | H |  |  | 315 | 316 (M+1) |

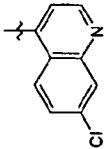
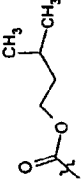

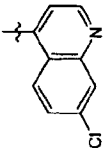
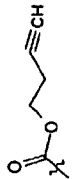

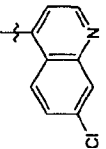
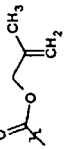
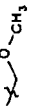
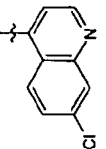

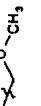
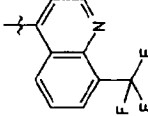


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 137 |  | H |  |  | 315 | 316 (M+1) |
| 138 |  | H |  |  | 315 | 316 (M+1) |
| 139 |  | H |  |  | 375 | 376 (M+1) |
| 140 |  | H |  |  | 345 | 346 (M+1) |

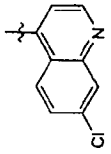
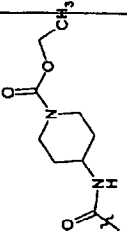

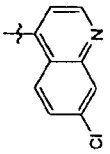
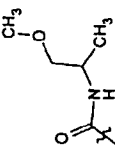

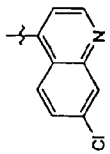
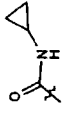

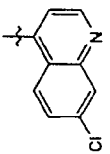
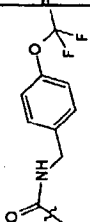

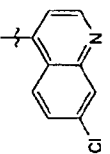
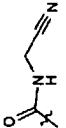

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 141 | | H | | | 341 | 342 (M+1) |
| 142 | | H | | | 345 | 346 (M+1) |
| 143 | | H | | | 339 | 340 (M+1) |
| 144 | | H | | | 375 | 376 (M+1) |

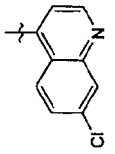
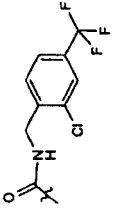

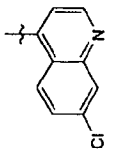
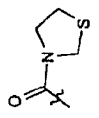

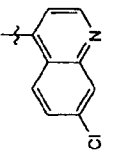
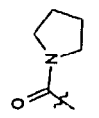

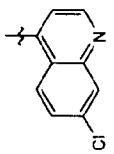
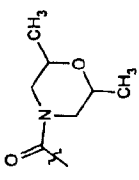

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 145 |  | H |  |  | 330 | 331 (M+1) |
| 146 |  | H |  |  | 335 | |
| 147 |  | H |  |  | 335 | |
| 148 |  | H |  |  | 335 | |

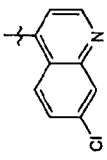
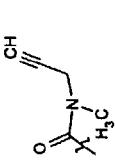

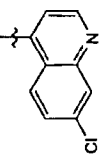
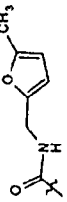

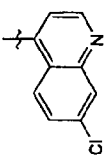
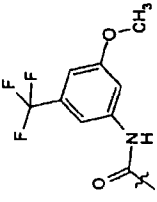

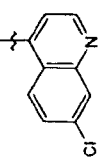

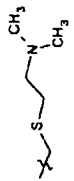
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 149 |  | H |  |  | 359 | 360 (M+1) |
| 150 |  | H |  |  | 371 | 372 (M+1) |
| 151 |  | H |  |  | 359 | 360 (M+1) |
| 152 |  | H |  |  | 363 | 364 (M+1) |
| 153 |  | H |  |  | 388 | 389 (M+1) |

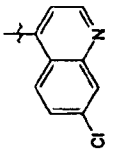
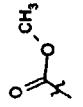
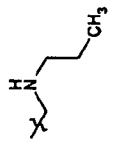
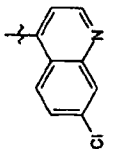
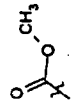
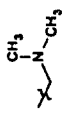
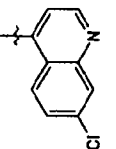
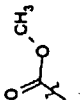
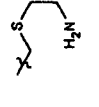
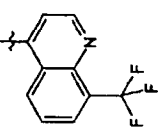
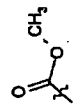
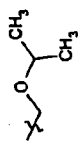
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 154 |  | H |  |  | 375 | 376 (M+1) |
| 155 |  | H |  |  | 389 | 390 (M+1) |
| 156 |  | H |  |  | 391 | 392 (M+1) |
| 157 |  | H |  |  | 369 | 370 (M+1) |
| 158 |  | H |  |  | 385 | 386 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|--|--------------------|-------------------|
| 159 |  | H |  |  | 387 | 388 (M+1) |
| 160 |  | H |  |  | 369 | 370 (M+1) |
| 161 |  | H |  |  | 371 | 372 (M+1) |
| 162 |  | H |  |  | 373 | 374 (M+1) |
| 163 |  |  |  | H | 394 | 395 (M+1) |

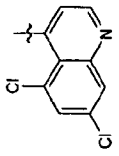
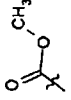

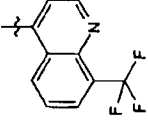
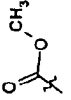
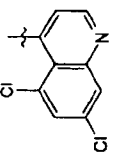
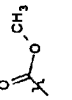
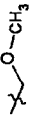
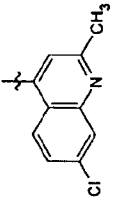
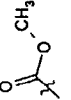
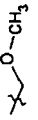
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 164 |  | H |  |  | 471 | 472 (M+1) |
| 165 |  | H |  |  | 388 | 389 (M+1) |
| 166 |  | H |  |  | 356 | 357 (M+1) |
| 167 |  | H |  |  | 490 | 491 (M+1) |
| 168 |  | H |  |  | 355 | 356 (M+1) |

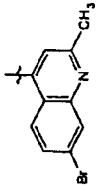
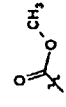

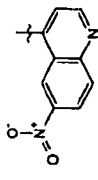
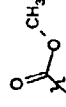

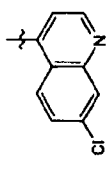
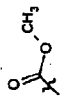
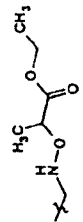
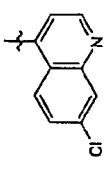

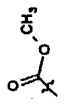
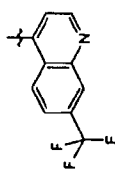
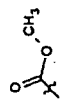
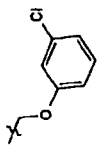
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 169 |  | H |  |  | 508 | 509 (M+1) |
| 170 |  | H |  |  | 388 | 389 (M+1) |
| 171 |  | H |  |  | 370 | 371 (M+1) |
| 172 |  | H |  |  | 414 | 415 (M+1) |

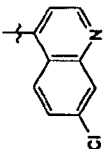

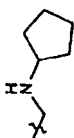
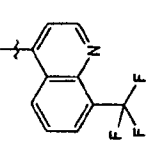
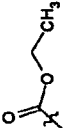
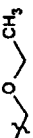
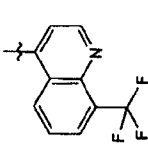

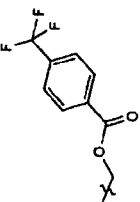
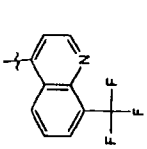

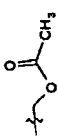
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 173 |  | H |  |  | 368 | 369 (M+1) |
| 174 |  | H |  |  | 410 | 411 (M+1) |
| 175 |  | H |  |  | 490 | 491 (M+1) |
| 176 |  | H |  |  | 404 | 405 (M+1) |

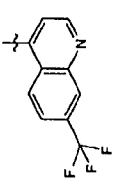
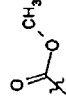

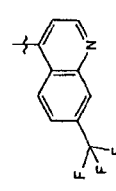
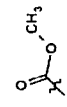
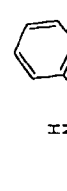
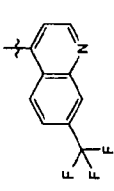
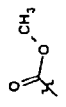
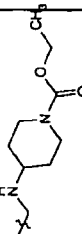
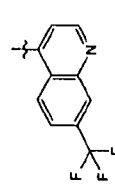
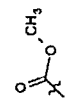

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 177 |  | H |  |  | 358 | 359 (M+1) |
| 178 |  | H |  |  | 344 | 345 (M+1) |
| 179 |  | H |  |  | 376 | 377 (M+1) |
| 180 |  | H |  |  | 393 | |

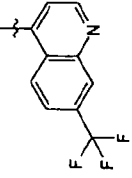
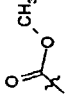
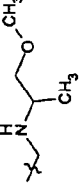
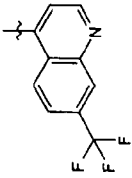
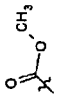
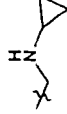
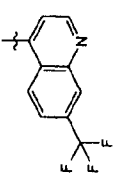
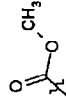
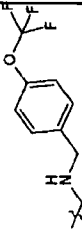
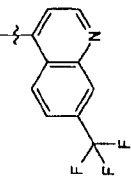

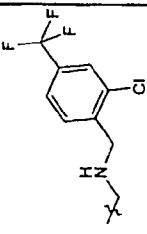
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 181 | | H | | | 379 | |
| 182 | | H | | | 345 | |
| 183 | | H | | | 413 | |
| 184 | | H | | | 413 | |

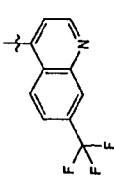
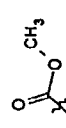
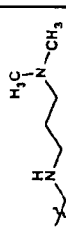
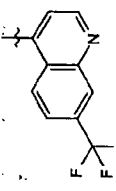
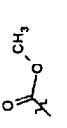
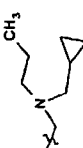
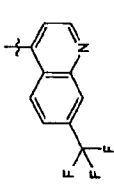
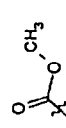

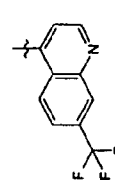
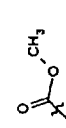

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|------------------|---|---|--------------------|-------------------|
| 185 |  | H |  |  | 413 | |
| 186 |  | H ₃ C |  | H | 335 | |
| 187 |  | H |  |  | 365 | 366 (M+1) |
| 188 |  | H |  |  | 345 | 346 (M+1) |

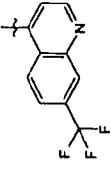

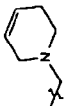
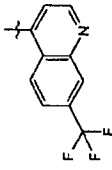

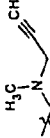
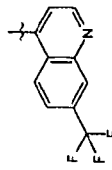

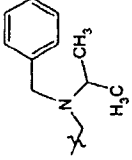
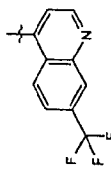

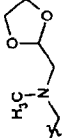
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|--|---|---|--------------------|-------------------|
| 189 |  | H |  |  | 389 | 390 (M+1) |
| 190 |  | H |  |  | 342 | 343 (M+1) |
| 191 |  | H |  |  | 432 | 433 (M+1) |
| 192 |  |  |  | H | 301 | |
| 193 |  | H |  |  | 461 | |

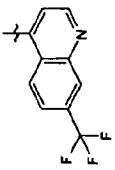

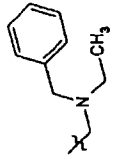
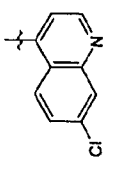
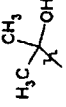
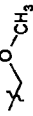
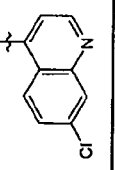
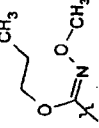
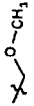
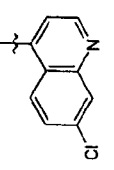
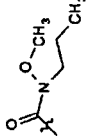

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 194 |  | H |  |  | 384 | |
| 195 |  | H |  |  | 393 | |
| 196 |  | H |  |  | 523 | 524 (M+1) |
| 197 |  | H |  |  | 393 | 394 (M+1) |

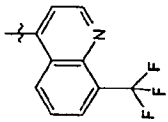

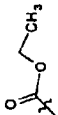
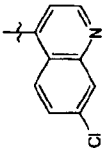
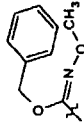
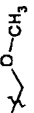
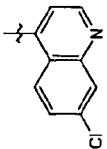
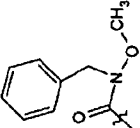
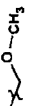
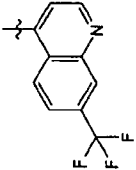
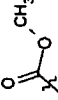
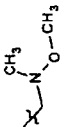
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 198 |  | H |  |  | 463 | 462 (M-1) |
| 199 |  | H |  |  | 441 | 442 (M+1) |
| 200 |  | H |  |  | 505 | 506 (M+1) |
| 201 |  | H |  |  | 475 | 476 (M+1) |

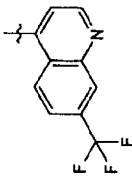

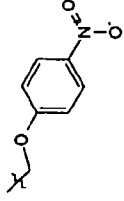
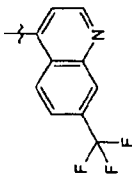

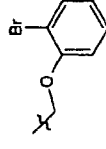
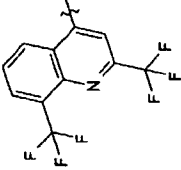


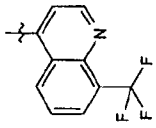


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 202 |  | H |  |  | 422 | 423 (M+1) |
| 203 |  | H |  |  | 390 | 391 (M+1) |
| 204 |  | H |  |  | 524 | 525 (M+1) |
| 205 |  | H |  |  | 542 | 541 (M-1) |

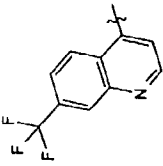

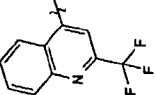

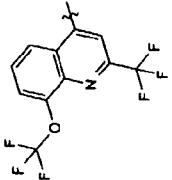

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 206 |  | H |  |  | 435 | 434 (M-1) |
| 207 |  | H |  |  | 446 | 447 (M+1) |
| 208 |  | H |  |  | 422 | 423 (M+1) |
| 209 |  | H |  |  | 404 | 405 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 210 |  | H |  |  | 416 | 417 (M+1) |
| 211 |  | H |  |  | 402 | 403 (M+1) |
| 212 |  | H |  |  | 482 | 483 (M+1) |
| 213 |  | H |  |  | 450 | 451 (M+1) |

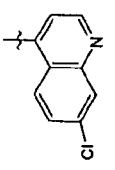
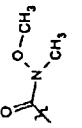

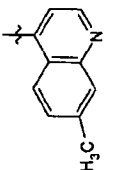
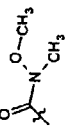

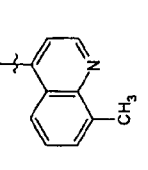
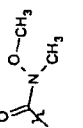

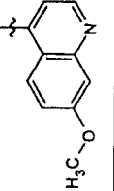
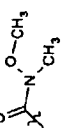

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 214 |  | H |  |  | 468 | 469 (M+1) |
| 215 |  | H |  |  | 331 | 332 (M+1) |
| 216 |  | H |  |  | 388 | 389 (M+1) |
| 217 |  | H |  |  | 388 | 389 (M+1) |

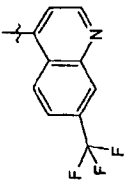
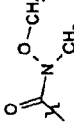
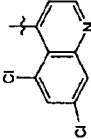
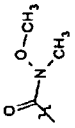
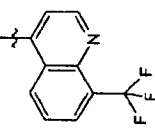
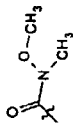
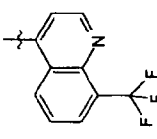
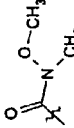
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 218 |  |  |  | H | 379 | 380 (M+1) |
| 219 |  | H |  |  | 436 | 437 (M+1) |
| 220 |  | H |  |  | 436 | 437 (M+1) |
| 221 |  | H |  |  | 394 | 395 (M+1) |

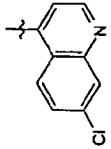
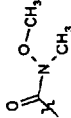
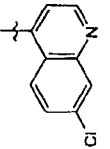
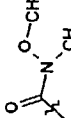
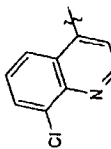
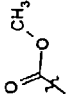
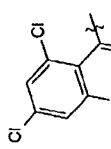
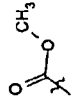
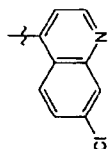

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 222 |  | H |  |  | 472 | 473 (M+1) |
| 223 |  | H |  |  | 505 | 506 (M+1) |
| 224 |  |  |  | H | 403 | 404 (M+1) |
| 225 |  |  |  | H | 335 | 336 (M+1) |

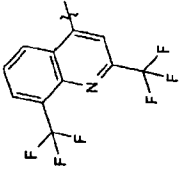
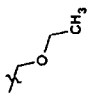
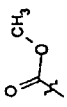
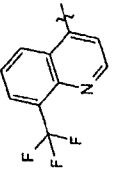

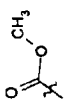
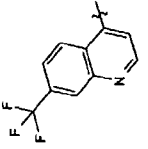
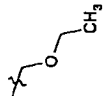
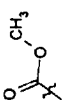
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|------------------|--|---|--------------------|-------------------|
| 226 |  | -X-CH_3 |  | H | 335 | 336 (M+1) |
| 227 |  | -X-CH_3 |  | H | 335 | 336 (M+1) |
| 228 |  | -X-CH_3 |  | H | 419 | 420 (M+1) |

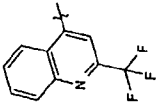


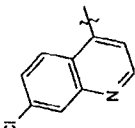
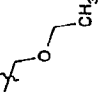

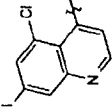
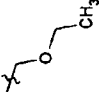

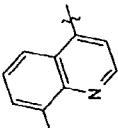
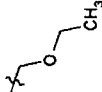

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|-----------------|---|---|--------------------|-------------------|
| 229 | | X-CH_3 | | H | 453 | 454 (M+1) |
| 230 | | X-CH_3 | | H | 349 | 350 (M+1) |
| 231 | | H | | | 394 | 395 (M+1) |

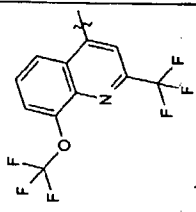
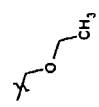
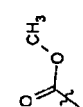
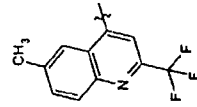
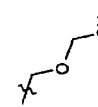
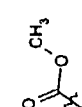
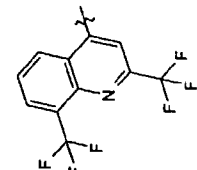
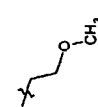
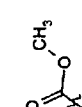
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 232 |  | H |  |  | 374 | 375 (M+1) |
| 233 |  | H |  |  | 354 | 355 (M+1) |
| 234 |  | H |  |  | 354 | 355 (M+1) |
| 235 |  | H |  |  | 370 | 371 (M+1) |

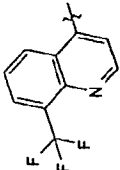


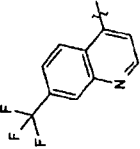


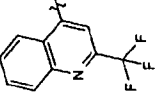


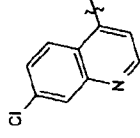


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|------------------------|--|-----------------|--------------------|-------------------|
| 236 |  | H |  | X-CH_3 | 364 | 365 (M+1) |
| 237 |  | H |  | X-CH_3 | 364 | 365 (M+1) |
| 238 |  | H |  | X-CH_3 | 364 | 365 (M+1) |
| 239 |  | $\text{H}_3\text{C-X}$ |  | H | 364 | 365 (M+1) |

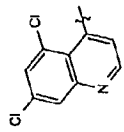
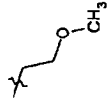
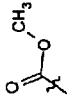
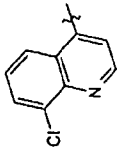
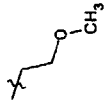
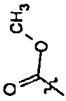
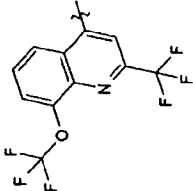
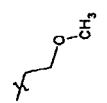
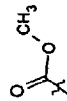
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|------------------------|---|-----------------|--------------------|-------------------|
| 240 |  | H |  | X-CH_3 | 330 | 331 (M+1) |
| 241 |  | $\text{H}_3\text{C-X}$ |  | H | 330 | 331 (M+1) |
| 242 |  | X-CH_3 |  | H | 301 | 302 (M+1) |
| 243 |  | X-CH_3 |  | H | 335 | 336 (M+1) |
| 244 |  | $\text{H}_3\text{C-X}$ |  | X-NH_2 | 283 | 284 (M+1) |

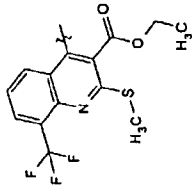
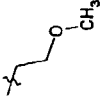

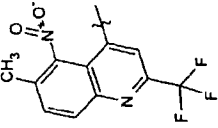
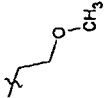

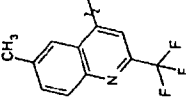
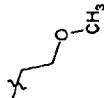

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 245 |  |  |  | H | 447 | 448 (M+1) |
| 246 |  |  |  | H | 379 | 380 (M+1) |
| 247 |  |  |  | H | 379 | 380 (M+1) |

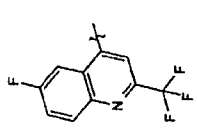
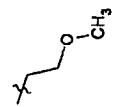
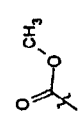
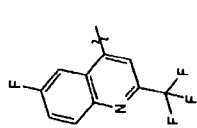

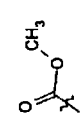
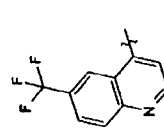
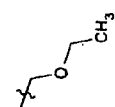
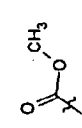
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 248 |  |  |  | H | 379 | 380 (M+1) |
| 249 |  |  |  | H | 345 | 346 (M+1) |
| 250 |  |  |  | H | 379 | 380 (M+1) |
| 251 |  |  |  | H | 345 | 346 (M+1) |

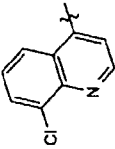
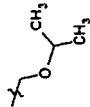
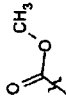
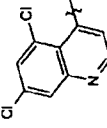
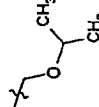
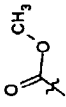
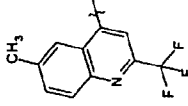
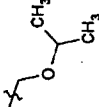
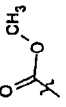
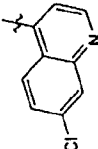
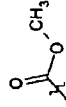
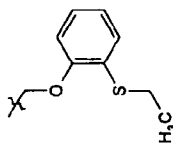
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|--|---|---|--------------------|-------------------|
| 252 |  |  |  | H | 463 | 464 (M+1) |
| 253 |  |  |  | H | 393 | 394 (M+1) |
| 254 |  |  |  | H | 447 | 448 (M+1) |

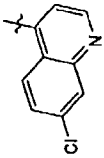
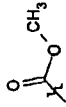
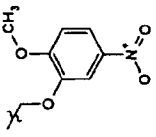
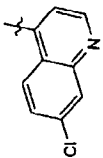

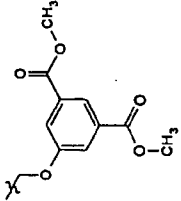
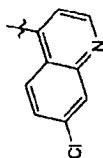

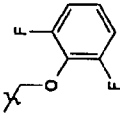
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 255 |  |  |  | H | 379 | 380 (M+1) |
| 256 |  |  |  | H | 379 | 380 (M+1) |
| 257 |  |  |  | H | 379 | 380 (M+1) |
| 258 |  |  |  | H | 345 | 346 (M+1) |

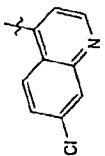
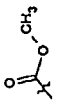
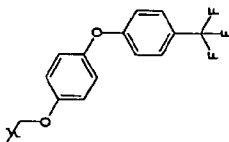
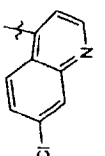
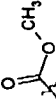
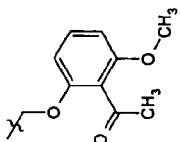
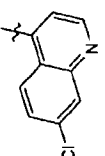
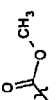
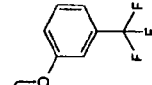
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 259 |  |  |  | H | 379 | 380 (M+1) |
| 260 |  |  |  | H | 345 | 346 (M+1) |
| 261 |  |  |  | H | 463 | 464 (M+1) |

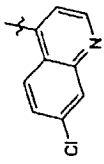

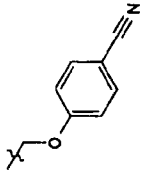
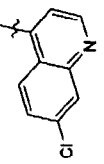

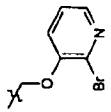
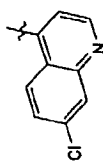

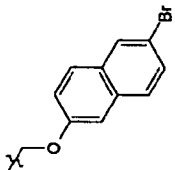
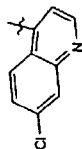

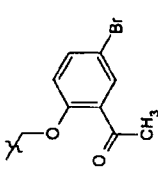
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 262 |  |  |  | H | 497 | 498 (M+1) |
| 263 |  |  |  | H | 438 | 437 (M-1) |
| 264 |  |  |  | H | 393 | 394 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 265 |  |  |  | H | 397 | 398 (M+1) |
| 266 |  |  |  | H | 353 | 354 (M+1) |
| 267 |  |  |  | H | 379 | 380 (M+1) |

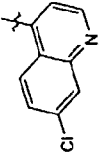
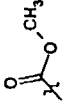
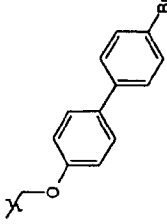
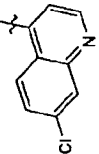
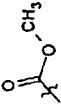
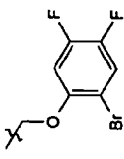
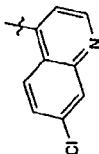

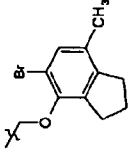
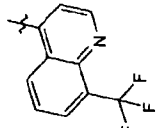

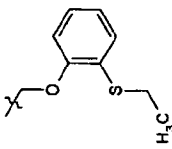
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 268 |  |  |  | H | 359 | 358 (M-1) |
| 269 |  |  |  | H | 393 | 394 (M+1) |
| 270 |  |  |  | H | 407 | 408 (M+1) |
| 271 |  | H |  |  | 453 | 454 (M+1) |

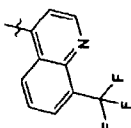

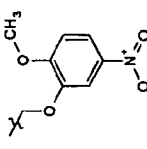
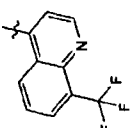

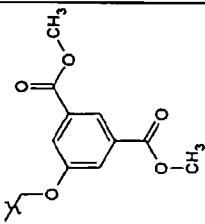
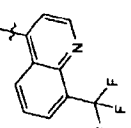

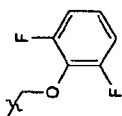
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 272 |  | H |  |  | 468 | 469 (M+1) |
| 273 |  | H |  |  | 509 | 510 (M+1) |
| 274 |  | H |  |  | 429 | 430 (M+1) |

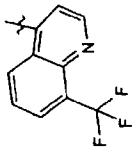

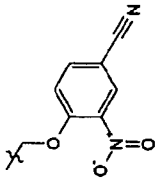
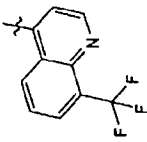

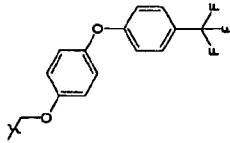
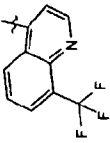

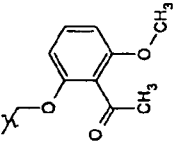
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 275 |  | H |  |  | 553 | 554 (M+1) |
| 276 |  | H |  |  | 465 | 466 (M+1) |
| 277 |  | H |  |  | 461 | 462 (M+1) |

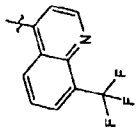

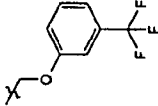
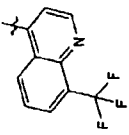

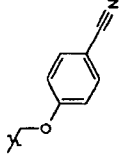
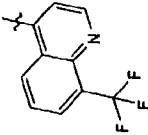

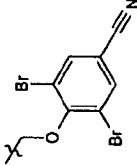
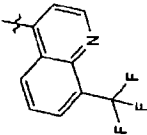

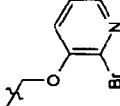
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 278 |  | H |  |  | 418 | 419 (M+1) |
| 279 |  | H |  |  | 472 | 473 (M+1) |
| 280 |  | H |  |  | 521 | 522 (M+1) |
| 281 |  | H |  |  | 513 | 514 (M+1) |

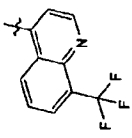
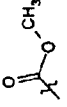
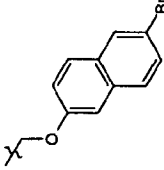
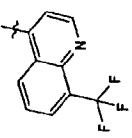
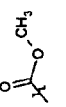
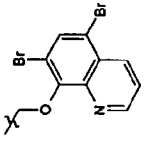
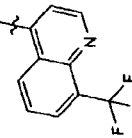
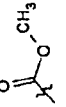
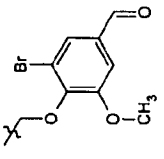
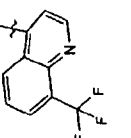
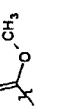
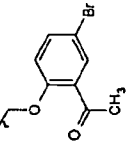
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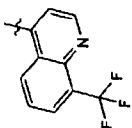
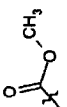
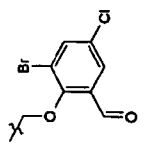
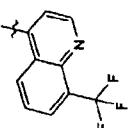
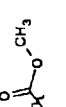
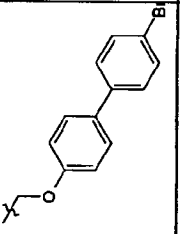
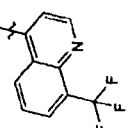
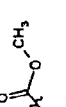
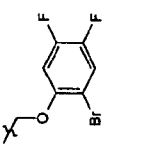
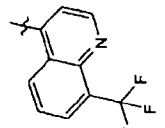
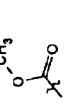
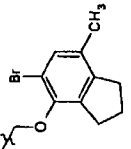
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 282 |  | H |  |  | 547 | 548 (M+1) |
| 283 |  | H |  |  | 507 | 508 (M+1) |
| 284 |  | H |  |  | 525 | 526 (M+1) |
| 285 |  | H |  |  | 487 | 488 (M+1) |

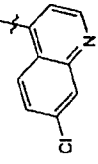


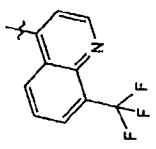



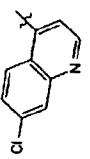
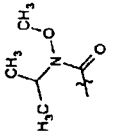
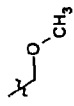
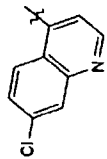
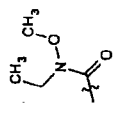
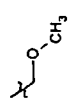
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 286 |  | H |  |  | 502 | 503 (M+1) |
| 287 |  | H |  |  | 543 | 544 (M+1) |
| 288 |  | H |  |  | 463 | 464 (M+1) |

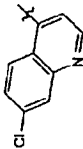
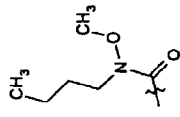
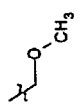
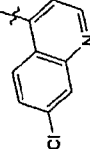
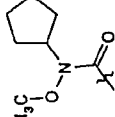
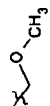
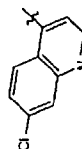
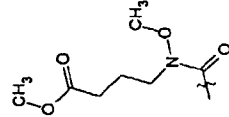
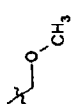
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 289 |  | H |  |  | 497 | 498 (M+1) |
| 290 |  | H |  |  | 587 | 588 (M+1) |
| 291 |  | H |  |  | 499 | 500 (M+1) |

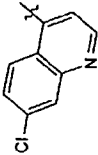
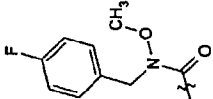

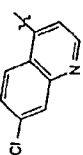
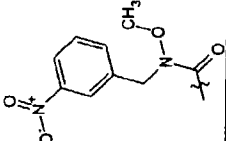

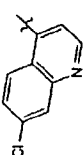
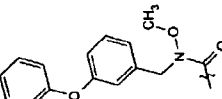

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 292 |  | H |  |  | 495 | 496 (M+1) |
| 293 |  | H |  |  | 452 | 453 (M+1) |
| 294 |  | H |  |  | 608 | 609 (M+1) |
| 295 |  | H |  |  | 506 | 507 (M+1) |

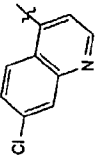
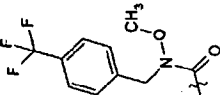

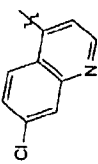
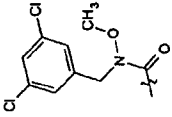

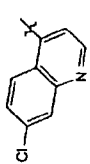
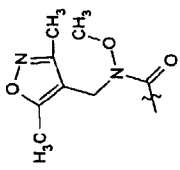

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 296 |  | H |  |  | 555 | 556 (M+1) |
| 297 |  | H |  |  | 634 | 635 (M+1) |
| 298 |  | H |  |  | 563 | 564 (M+1) |
| 299 |  | H |  |  | 547 | 548 (M+1) |

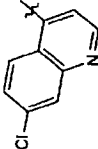
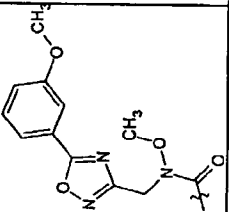

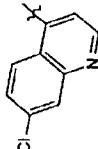
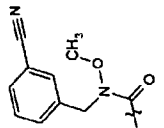

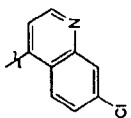
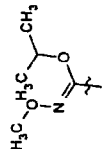

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 300 |  | H |  |  | 567 | 568 (M+1) |
| 301 |  | H |  |  | 581 | 582 (M+1) |
| 302 |  | H |  |  | 541 | 542 (M+1) |
| 303 |  | H |  |  | 559 | 560 (M+1) |

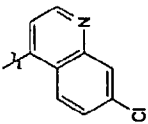
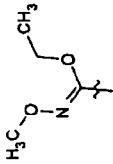

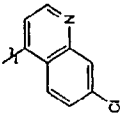
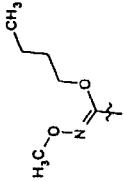

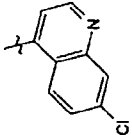
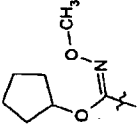

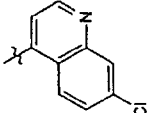
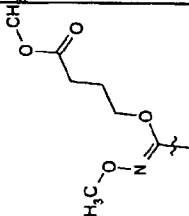

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 304 |  |  |  | H | 268 | 269 (M+1) |
| 305 |  |  |  |  | 317 | 318 (M+1) |
| 306 |  | H |  |  | 388 | 389 (M+1) |
| 307 |  | H |  |  | 374 | 375 (M+1) |

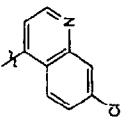
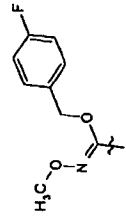
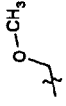
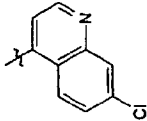
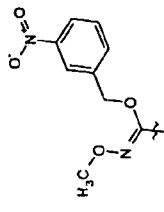
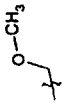
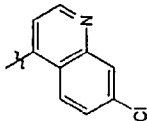
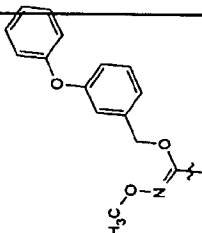
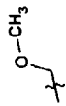
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 308 |  | H |  |  | 402 | 403 (M+1) |
| 309 |  | H |  |  | 414 | 415 (M+1) |
| 310 |  | H |  |  | 446 | 447 (M+1) |

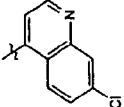
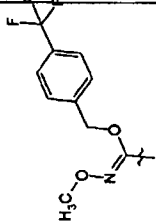

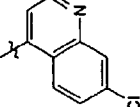
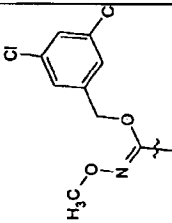

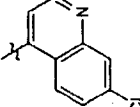
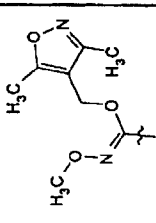

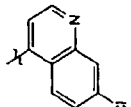
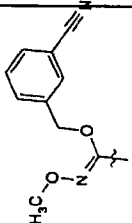

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 311 |  | H |  |  | 454 | 455 (M+1) |
| 312 |  | H |  |  | 481 | 482 (M+1) |
| 313 |  | H |  |  | 528 | 529 (M+1) |

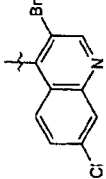


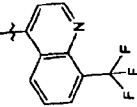

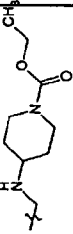
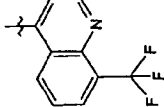


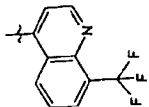

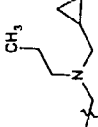
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 314 |  | H |  |  | 504 | 505 (M+1) |
| 315 |  | H |  |  | 504 | 505 (M+1) |
| 316 |  | H |  |  | 455 | 456 (M+1) |

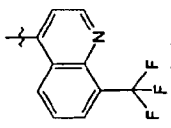

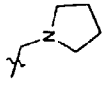
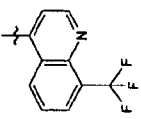
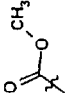
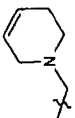
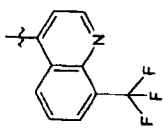
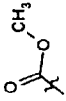
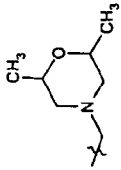
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 317 |  | H |  |  | 534 | 535 (M+1) |
| 318 |  | H |  |  | 461 | 462 (M+1) |
| 319 |  | H |  |  | 388 | 389 (M+1) |

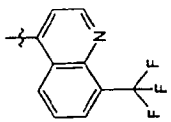

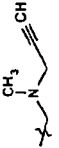
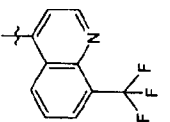

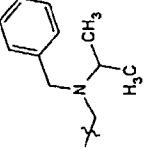
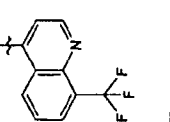

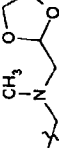
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 320 |  | H |  |  | 374 | 375 (M+1) |
| 321 |  | H |  |  | 402 | 403 (M+1) |
| 322 |  | H |  |  | 414 | 415 (M+1) |
| 323 |  | H |  |  | 446 | 447 (M+1) |

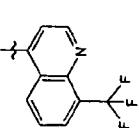

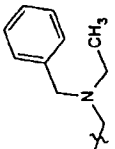
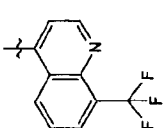

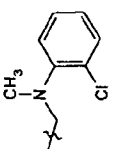
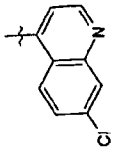

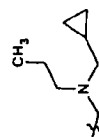
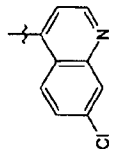

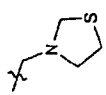
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 324 |  | H |  |  | 454 | 455 (M+1) |
| 325 |  | H |  |  | 481 | 482 (M+1) |
| 326 |  | H |  |  | 528 | 529 (M+1) |

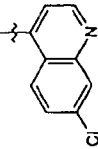

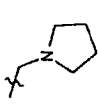
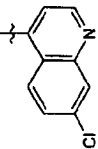
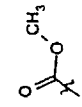
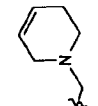
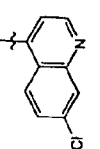
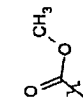
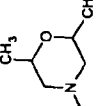
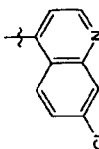
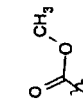
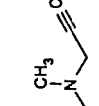
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 327 |  | H |  |  | 504 | 505 (M+1) |
| 328 |  | H |  |  | 504 | 505 (M+1) |
| 329 |  | H |  |  | 455 | 456 (M+1) |
| 330 |  | H |  |  | 461 | 462 (M+1) |

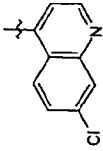

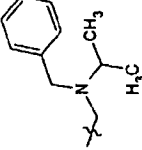
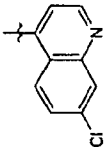

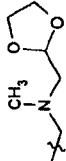
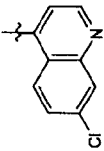

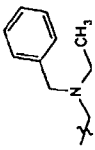
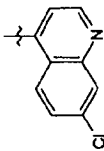

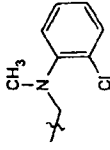
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|--------------------|-------------------|
| 331 |  |  |  | H | 409 | 410 (M+1) |
| 332 |  | H |  |  | 505 | 505 (M+1) |
| 333 |  | H |  |  | 390 | 390 (M+1) |
| 334 |  | H |  |  | 446 | 446 (M+1) |

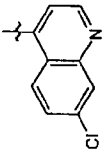
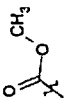
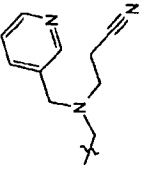
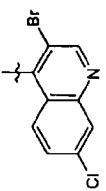

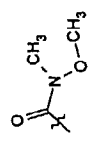
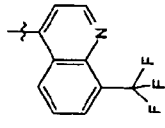
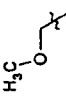

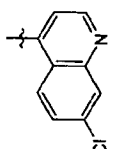

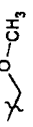
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 335 |  | H |  |  | 404 | 404 (M+1) |
| 336 |  | H |  |  | 416 | 416 (M+1) |
| 337 |  | H |  |  | 448 | 448 (M+1) |

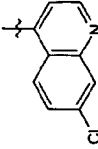

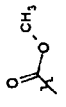
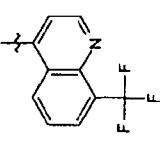
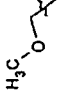

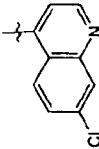

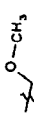
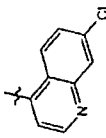
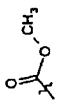
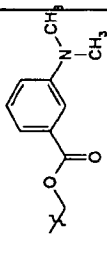
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 338 |  | H |  |  | 402 | 403 (M+1) |
| 339 |  | H |  |  | 482 | 481 (M-1) |
| 340 |  | H |  |  | 450 | 451 (M+1) |

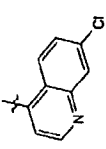

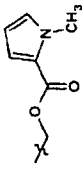
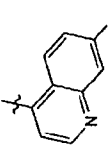
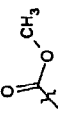
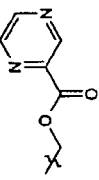
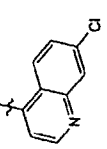
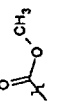
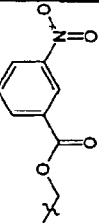
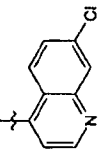
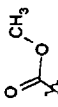
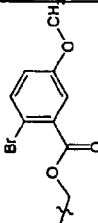
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 341 |  | H |  |  | 468 | 469 (M+1) |
| 342 |  | H |  |  | 474 | 475 (M+1) |
| 343 |  | H |  |  | 412 | 413 (M+1) |
| 344 |  | H |  |  | 388 | 389 (M+1) |

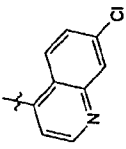

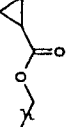
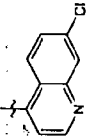

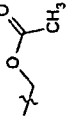
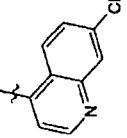

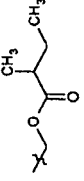
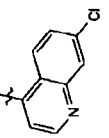

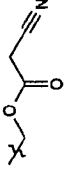
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 345 |  | H |  |  | 370 | 371 (M+1) |
| 346 |  | H |  |  | 382 | 383 (M+1) |
| 347 |  | H |  |  | 414 | 415 (M+1) |
| 348 |  | H |  |  | 368 | 369 (M+1) |

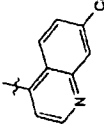

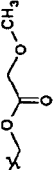
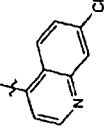

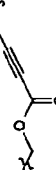
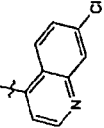


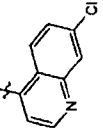

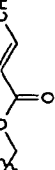
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 349 |  | H |  |  | 448 | 449 (M+1) |
| 350 |  | H |  |  | 416 | 417 (M+1) |
| 351 |  | H |  |  | 434 | 435 (M+1) |
| 352 |  | H |  |  | 440 | 441 (M+1) |

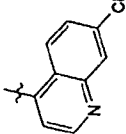

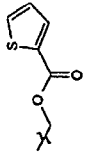
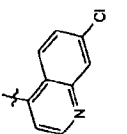

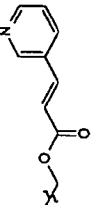
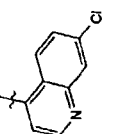

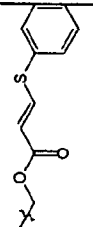
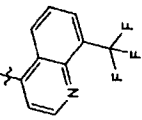

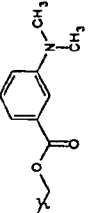
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 353 |  | H |  |  | 460 | 461 (M+1) |
| 354 |  |  |  | H | 438 | 439 (M+1) |
| 355 |  |  |  | H | 365 | 366 (M+1) |
| 356 |  | H |  |  | 303 | 304 (M+1) |

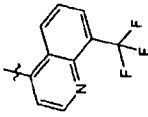

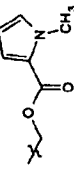
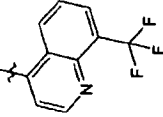

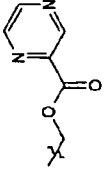
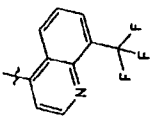
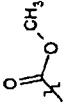
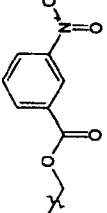
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 357 |  |  |  | H | 457 | 458 (M+1) |
| 358 |  |  |  | H | 406 | 407 (M+1) |
| 359 |  | H |  |  | 298 | 299 (M+1) |
| 360 |  | H |  |  | 464 | 465 (M+1) |

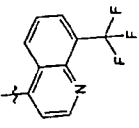
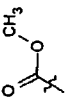
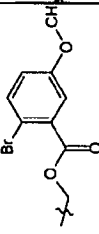
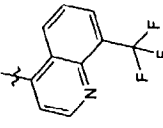

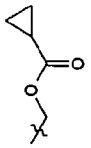
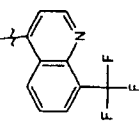

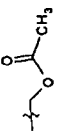
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 361 |  | H |  |  | 424 | 425 (M+1) |
| 362 |  | H |  |  | 423 | 424 (M+1) |
| 363 |  | H |  |  | 466 | 467 (M+1) |
| 364 |  | H |  |  | 529 | 530 (M+1) |

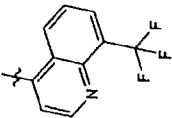

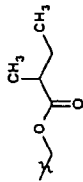
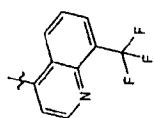

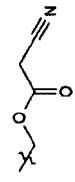
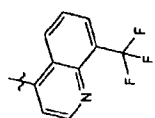

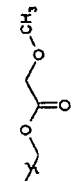
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 365 |  | H |  |  | 385 | 386 (M+1) |
| 366 |  | H |  |  | 359 | 360 (M+1) |
| 367 |  | H |  |  | 401 | 402 (M+1) |
| 368 |  | H |  |  | 384 | 385 (M+1) |

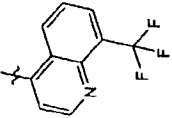
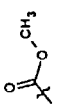
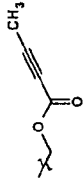
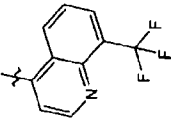
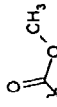

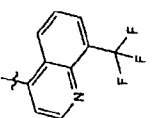
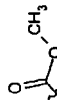
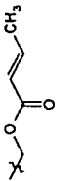
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 369 |  | H |  |  | 389 | 390 (M+1) |
| 370 |  | H |  |  | 383 | 384 (M+1) |
| 371 |  | H |  |  | 429 | 430 (M+1) |
| 372 |  | H |  |  | 385 | 386 (M+1) |

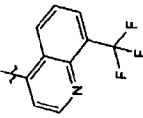
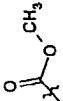
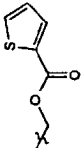
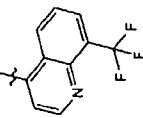
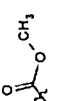
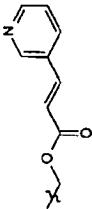
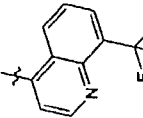
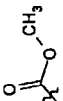

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 373 |  | H |  |  | 427 | 428 (M+1) |
| 374 |  | H |  |  | 448 | 449 (M+1) |
| 375 |  | H |  |  | 479 | 480 (M+1) |
| 376 |  | H |  |  | 498 | 497 (M-1) |

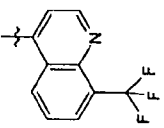


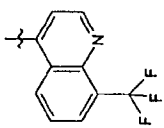

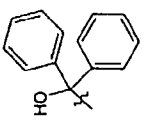
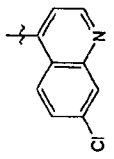
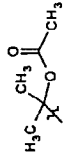
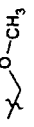
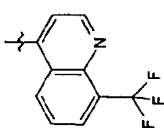

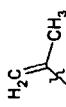
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 377 |  | H |  |  | 458 | 457 (M-1) |
| 378 |  | H |  |  | 457 | 458 (M+1) |
| 379 |  | H |  |  | 500 | 501 (M+1) |

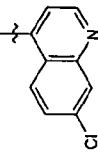
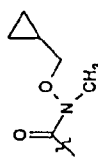
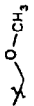
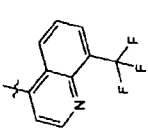

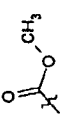

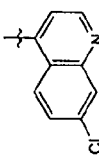


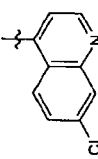


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 380 |  | H |  |  | 563 | 564 (M+1) |
| 381 |  | H |  |  | 419 | 420 (M+1) |
| 382 |  | H |  |  | 393 | 394 (M+1) |

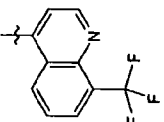


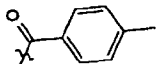
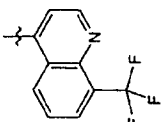



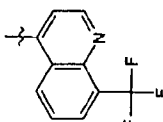



| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 383 |  | H |  |  | 435 | 434 (M-1) |
| 384 |  | H |  |  | 418 | 419 (M+1) |
| 385 |  | H |  |  | 423 | 422 (M-1) |

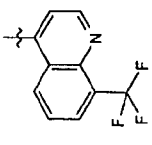


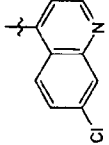


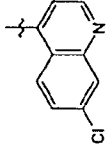


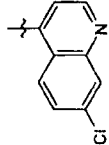


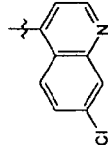


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 386 |  | H |  |  | 417 | 418 (M+1) |
| 387 |  | H |  |  | 463 | 462 (M-1) |
| 388 |  | H |  |  | 419 | 418 (M-1) |

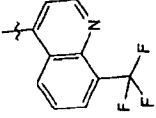

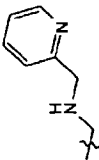
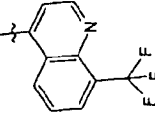


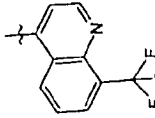

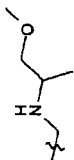
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 389 |  | H |  |  | 461 | 460 (M-1) |
| 390 |  | H |  |  | 482 | 483 (M+1) |
| 391 |  | H |  |  | 513 | 514 (M+1) |

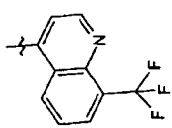

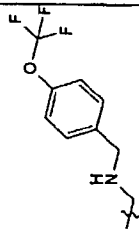
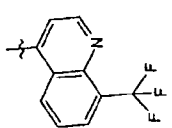


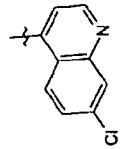


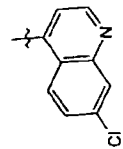

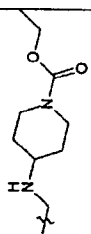
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 392 |  |  |  | H | 393 | 394 (M+1) |
| 393 |  |  |  | H | 489 | 490 (M+1) |
| 394 |  | H |  |  | 373 | 374 (M+1) |
| 395 |  |  |  | H | 347 | 348 (M+1) |

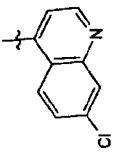

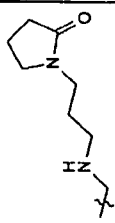
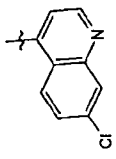

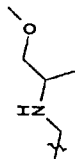
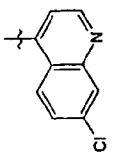

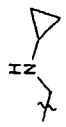
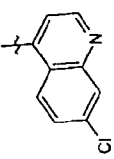

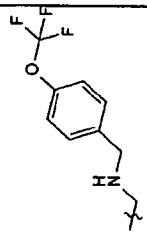
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 396 |  | H |  |  | 400 | 401 (M+1) |
| 397 |  |  |  |  | 379 | 380 (M+1) |
| 398 |  |  |  | H | 301 | 302 (M+1) |
| 399 |  | H |  |  | 315 | 316 (M+1) |

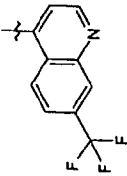

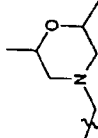
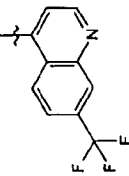

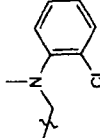
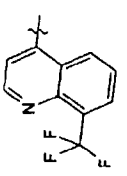


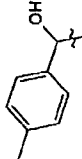
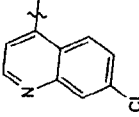



| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 400 |  |  |  |  | 483 | 485 (M+2) |
| 401 |  |  |  |  | 409 | 410 (M+1) |
| 402 |  |  |  |  | 423 | 424 (M+1) |

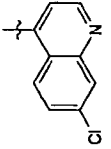
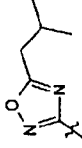

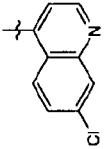


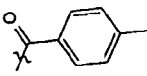
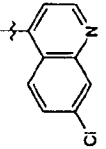
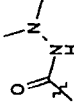

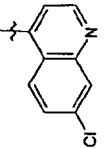
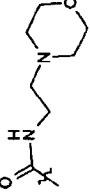

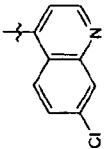


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|--|--|---|--------------------|-------------------|
| 403 |  |  |  | H | 378 | 379 (M+1) |
| 404 |  |  |  | H | 321 | 322 (M) |
| 405 |  | H |  |  | 331 | 332 (M+1) |
| 406 |  |  |  | H | 325 | 326 (M+1) |
| 407 |  | H |  |  | 355 | 356 (M+1) |

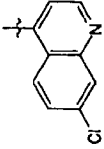
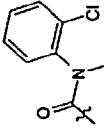

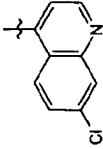
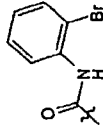

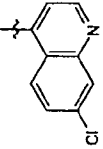
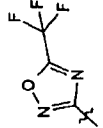

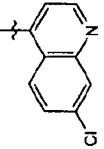
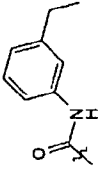
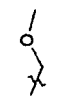
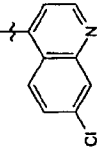



| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|--|--------------------|-------------------|
| 408 |  | H |  |  | 441 | |
| 409 |  | H |  |  | 475 | |
| 410 |  | H |  |  | 422 | |

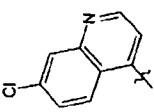
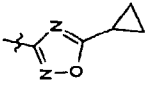

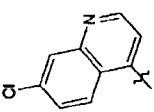
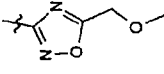

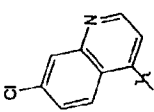
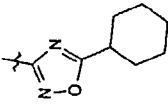

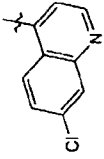
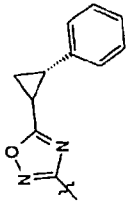

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 411 |  | H |  |  | 524 | |
| 412 |  | H |  |  | 389 | |
| 413 |  | H |  |  | 429 | |
| 414 |  | H |  |  | 471 | |

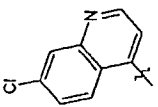
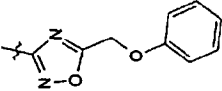

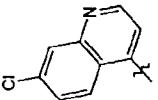
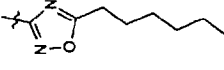

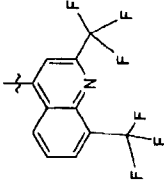


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 415 |  | H |  |  | 441 | |
| 416 |  | H |  |  | 388 | |
| 417 |  | H |  |  | 356 | |
| 418 |  | H |  |  | 490 | |

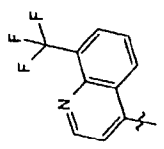
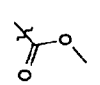
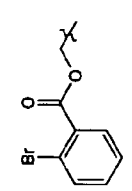
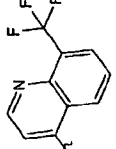
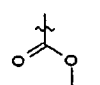
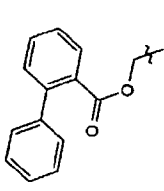
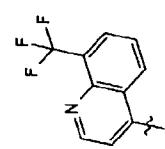

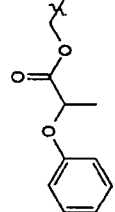
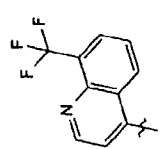

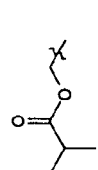
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 419 |  | H |  |  | 448 | |
| 420 |  | H |  |  | 474 | |
| 421 |  |  |  |  | 485 | 486 (M+1) |
| 422 |  |  |  |  | 457 | 458 (M+1) |

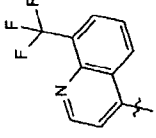

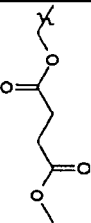
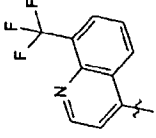

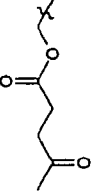
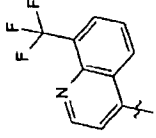

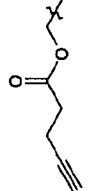
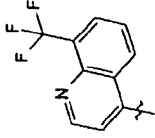

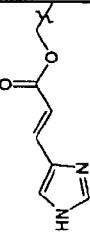
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 423 |  | H |  |  | 397 | 398 (M+1) |
| 424 |  |  |  |  | 449 | 451 (M+2) |
| 425 |  | H |  |  | 359 | 360 (M+1) |
| 426 |  | H |  |  | 429 | 430 (M+1) |
| 427 |  | H |  |  | 330 | 331 (M+1) |

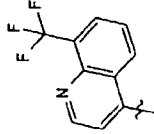

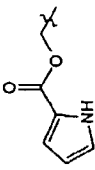
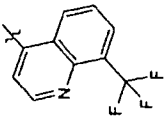

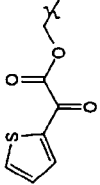
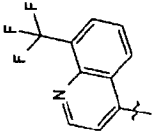

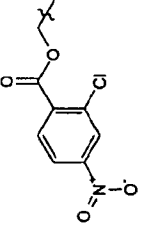
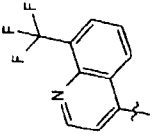

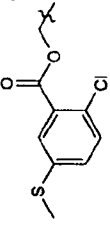
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 428 |  | H |  |  | 440 | 441 (M+1) |
| 429 |  | H |  |  | 470 | 471 (M+1) |
| 430 |  | H |  |  | 409 | 412 (M+3) |
| 431 |  | H |  |  | 420 | 421 (M+1) |
| 432 |  |  |  |  | 377 | 378 (M+1) |

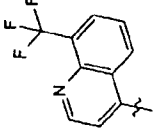

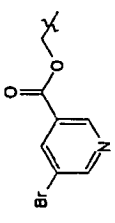
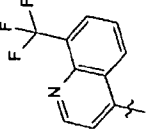

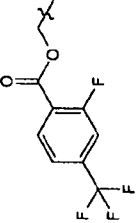
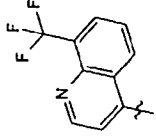

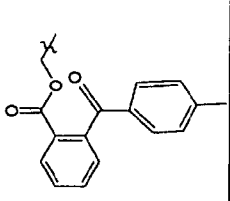
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 433 |  | H |  |  | 381 | 382 (M+1) |
| 434 |  | H |  |  | 385 | 386 (M+1) |
| 435 |  | H |  |  | 423 | 424 (M+1) |
| 436 |  | H |  |  | 457 | 458 (M+1) |

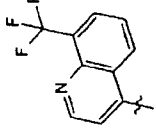

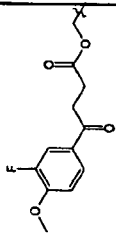
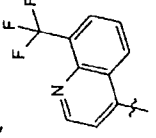

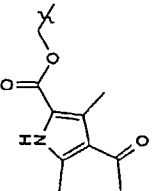
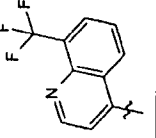

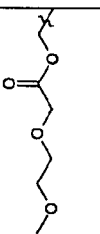
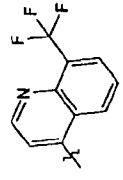

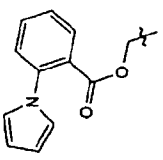
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 437 |  | H |  |  | 447 | 448 (M+1) |
| 438 |  | H |  |  | 425 | 426 (M+1) |
| 439 |  |  |  | H | 462 | |

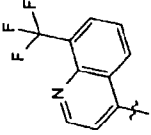

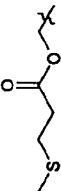
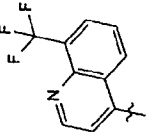

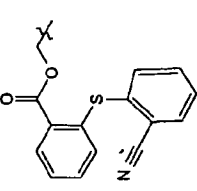
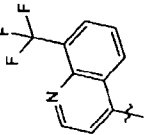

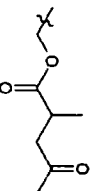
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 440 |  | H |  |  | 533 | |
| 441 |  | H |  |  | 531 | |
| 442 |  | H |  |  | 499 | |
| 443 |  | H |  |  | 421 | |

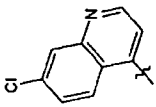
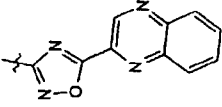

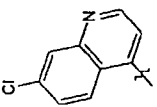
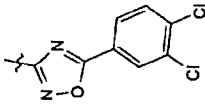

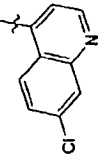
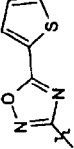

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 444 |  | H |  |  | 465 | |
| 445 |  | H |  |  | 449 | |
| 446 |  | H |  |  | 431 | |
| 447 |  | H |  |  | 471 | |

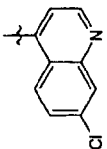



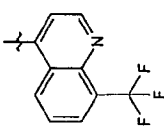
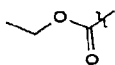
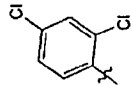
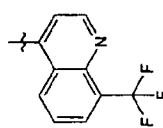


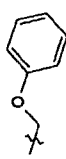
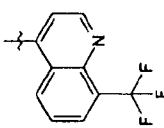


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 448 |  | H |  |  | 444 | |
| 449 |  | H |  |  | 489 | |
| 450 |  | H |  |  | 534 | |
| 451 |  | H |  |  | 535 | |

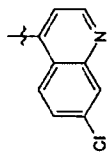


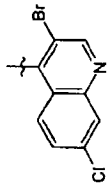


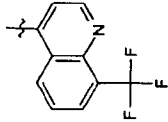


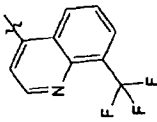

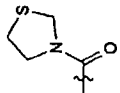
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 452 |  | H |  |  | 534 | |
| 453 |  | H |  |  | 541 | |
| 454 |  | H |  |  | 573 | |

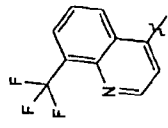

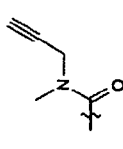
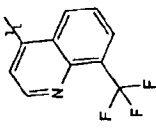

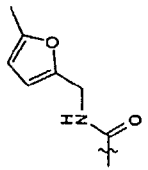
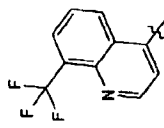

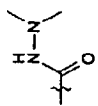
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 455 |  | H |  |  | 559 | |
| 456 |  | H |  |  | 514 | |
| 457 |  | H |  |  | 467 | |
| 458 |  | H |  |  | 520 | |

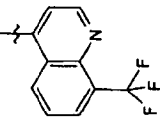


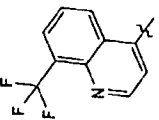

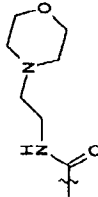
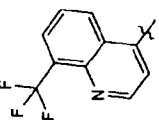


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 459 |  | H |  |  | 453 | |
| 460 |  | H |  |  | 588 | |
| 461 |  | H |  |  | 463 | |

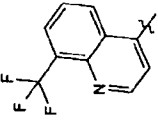

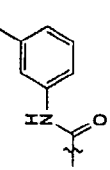
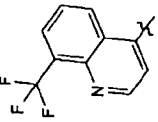

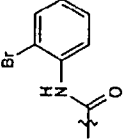
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|--|--------------------|-------------------|
| 462 |  | H |  |  | 469 | 470 (M+1) |
| 463 |  | H |  |  | 485 | 486 (M+1) |
| 464 |  | H |  |  | 423 | 424 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 465 |  |  |  |  | 393 | 394 (M+1) |
| 466 |  |  |  | H | 479 | 480 (M+1) |
| 467 |  |  |  |  | 441 | 443 (M+2) |
| 468 |  |  |  | H | 328 | 330 (M+2) |

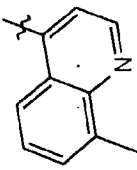

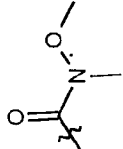
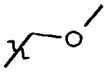
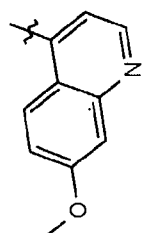

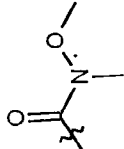
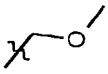
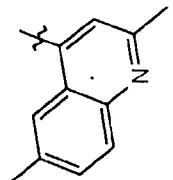

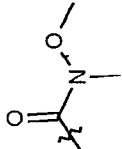
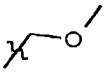
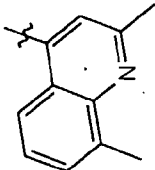

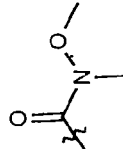
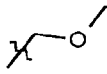
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 469 |  |  |  | H | 294 | 295 (M+1) |
| 470 |  | H |  |  | 409 | 412 (M+3) |
| 471 |  |  |  | H | 332 | 333 (M+1) |
| 472 |  |  |  | H | 422 | 423 (M+1) |

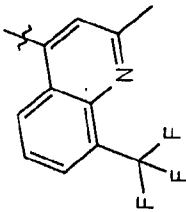

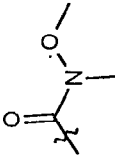
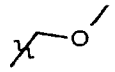
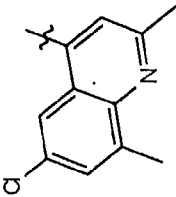

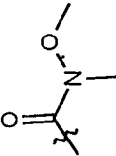
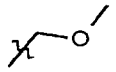
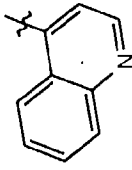

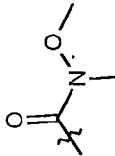
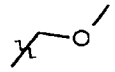
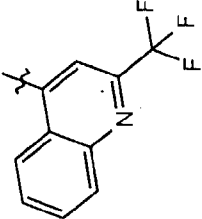

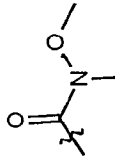
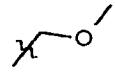
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|--------------------|-------------------|
| 473 |  |  |  | H | 402 | 403 (M+1) |
| 474 |  |  |  | H | 444 | 445 (M+1) |
| 475 |  |  |  | H | 393 | 394 (M+1) |

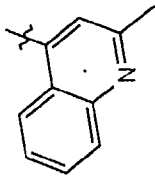

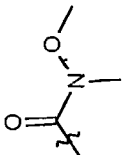
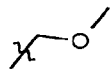
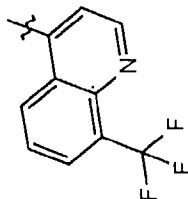

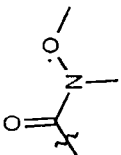
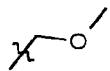
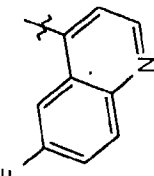

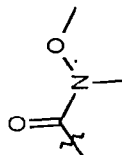
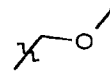
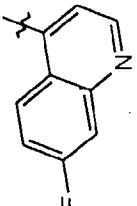

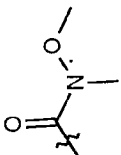
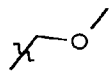
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|--------------------|-------------------|
| 476 |  |  |  | H | 365 | |
| 477 |  |  |  | H | 463 | 464 (M+1) |
| 478 |  |  |  | H | 364 | 365 (M+1) |

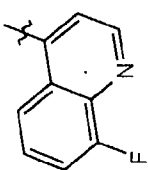

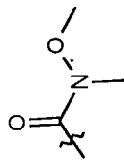
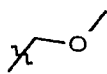
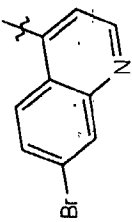

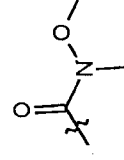
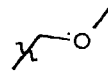
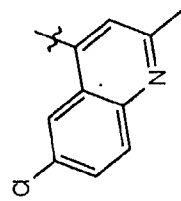

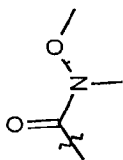
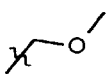
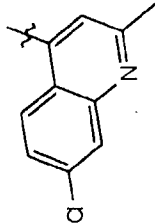

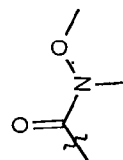
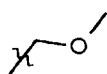
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|--------------------|-------------------|
| 479 |  |  |  | H | 454 | 455 (M+1) |
| 480 |  |  |  | H | 504 | 503 (M-1) |

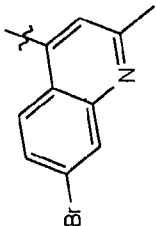

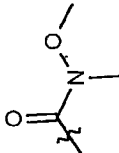
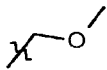
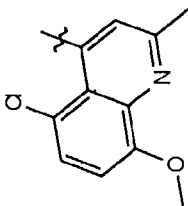

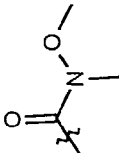
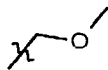
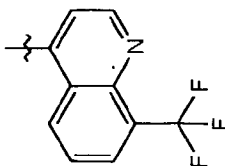

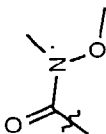

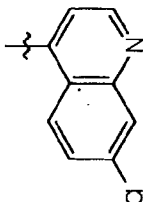

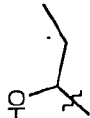

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 481 | | | | | 367 | |
| 482 | | | | | 354 | 355 (M+1) |
| 483 | | | | | 354 | 355 (M+1) |
| 484 | | | | | 388 | 389 (M+1) |

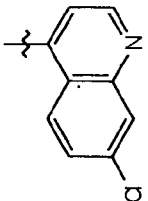

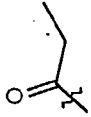
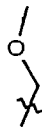
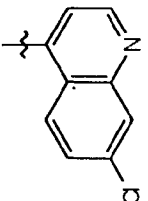

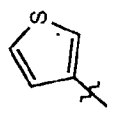

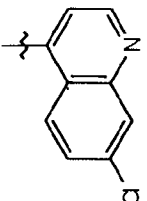

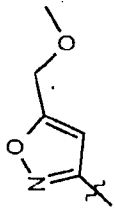

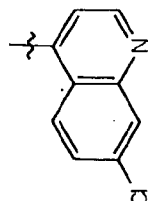

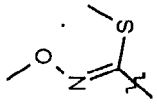
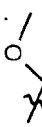
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 485 |  |  |  |  | 340 | 341 (M+1) |
| 486 |  |  |  |  | 356 | 357 (M+1) |
| 487 |  |  |  |  | 354 | 355 (M+1) |
| 488 |  |  |  |  | 354 | 355 (M+1) |

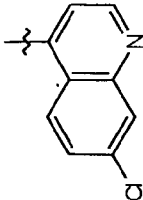

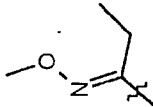

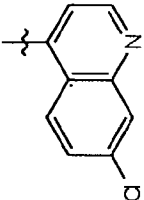

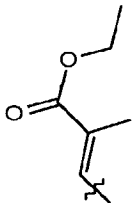

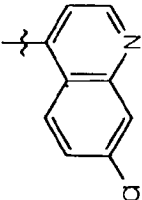

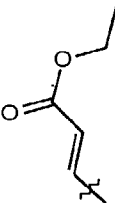

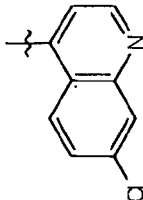

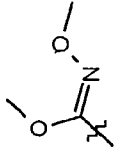

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 489 |  |  |  |  | 408 | 409 (M+1) |
| 490 |  |  |  |  | 388 | 389 (M+1) |
| 491 |  |  |  |  | 326 | 326 (M+1) |
| 492 |  |  |  |  | 394 | 395 (M+1) |

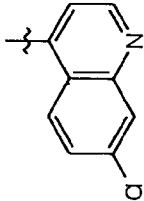

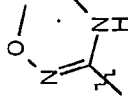

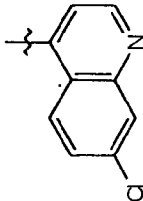

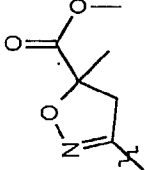

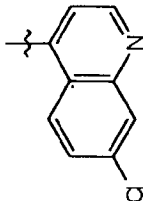

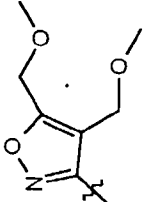
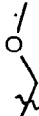
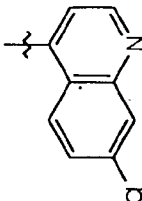

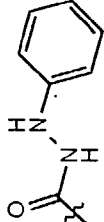

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 493 |  |  |  |  | 340 | 341 (M+1) |
| 494 |  |  |  |  | 394 | 395 (M+1) |
| 495 |  |  |  |  | 344 | 345 (M+1) |
| 496 |  |  |  |  | 344 | 345 (M+1) |

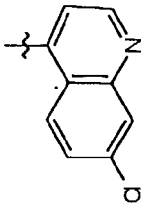

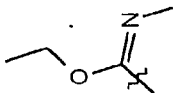

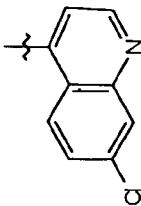

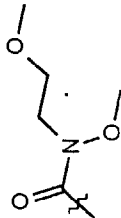

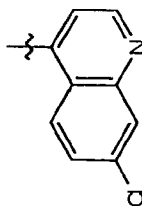

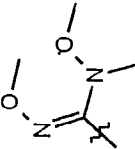

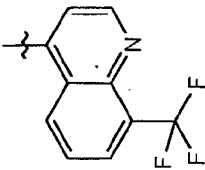
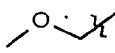
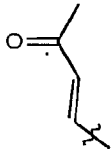

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 497 |  |  |  |  | 344 | 345 (M+1) |
| 498 |  |  |  |  | 404 | 405 (M+1) |
| 499 |  |  |  |  | 374 | 375 (M+1) |
| 500 |  |  |  |  | 374 | 375 (M+1) |

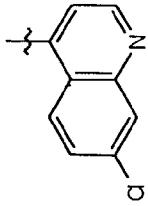

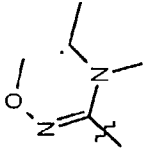

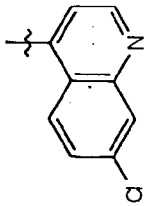



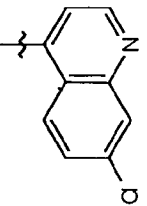

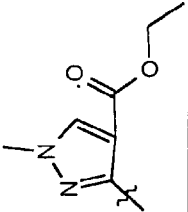
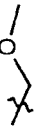
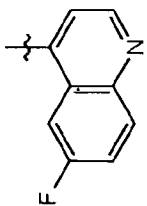

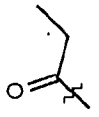

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 501 |  |  |  |  | 418 | 419 (M+1) |
| 502 |  |  |  |  | 404 | 405 (M+1) |
| 503 |  |  |  |  | 380 | |
| 504 |  |  |  |  | 331 | 332 (M+1) |

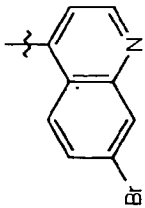

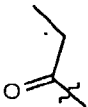
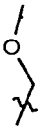
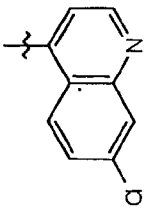

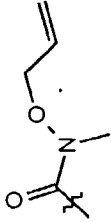

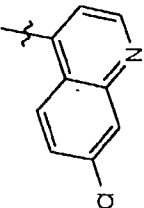

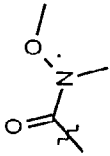

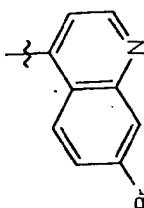

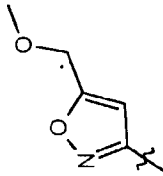

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 505 |  |  |  |  | 329 | 330 (M+1) |
| 506 |  |  |  |  | 355 | 356 (M+1) |
| 507 |  |  |  |  | 384 | 385 (M+1) |
| 508 |  |  |  |  | 376 | 377 (M+1) |

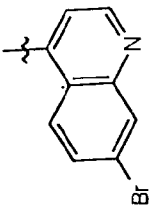

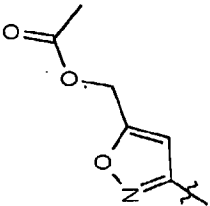
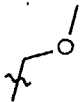
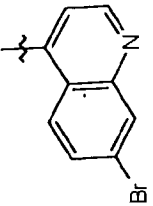

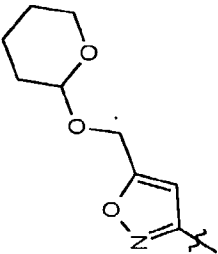
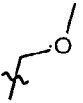
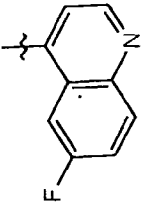

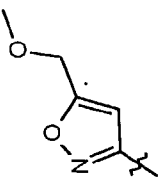
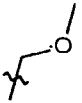
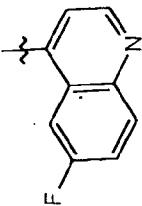

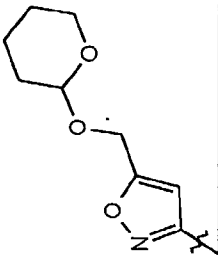
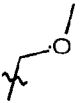
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 509 |  |  |  |  | 358 | |
| 510 |  |  |  |  | 385 | |
| 511 |  |  |  |  | 371 | |
| 512 |  |  |  |  | 360 | |

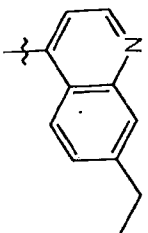

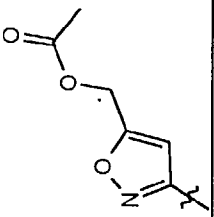
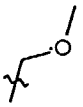
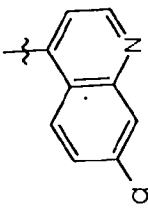

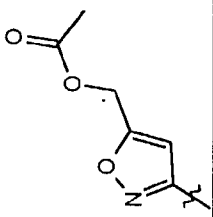
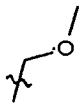
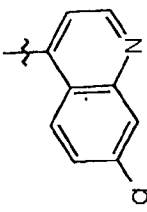

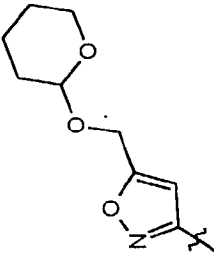
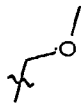
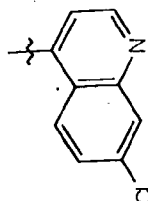

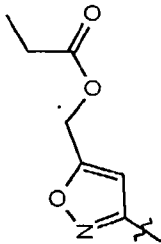
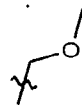
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 513 |  |  |  |  | 359 | 360 (M+1) |
| 514 |  |  |  |  | 414 | 415 (M+1) |
| 515 |  |  |  |  | 428 | 429 (M+1) |
| 516 |  |  |  |  | 407 | 409 (M+1) |

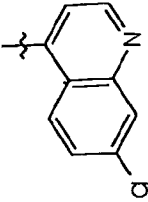

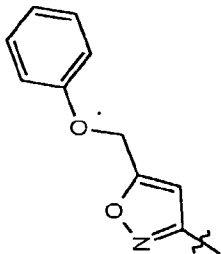

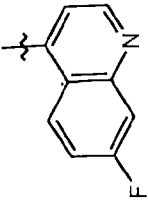

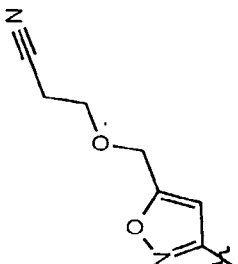

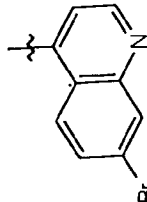

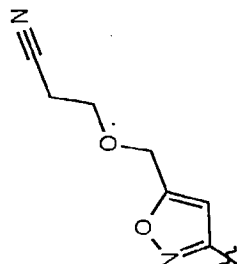

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 517 |  |  |  |  | 358 | 359 (M+1) |
| 518 |  |  |  |  | 404 | 405 (M+1) |
| 519 |  |  |  |  | 389 | 390 (M+1) |
| 520 |  |  |  |  | 375 | 376 (M+1) |

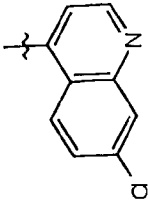

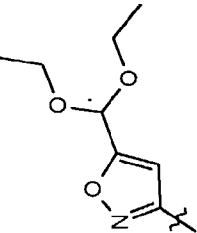
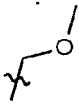
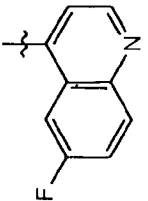

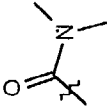
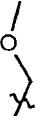
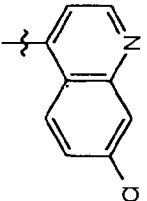

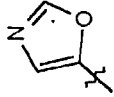

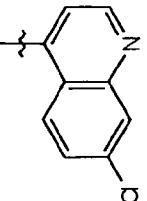

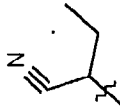

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 521 |  |  |  |  | 387 | 388 (M+1) |
| 522 |  |  |  |  | 313 | |
| 523 |  |  |  |  | 425 | 426 (M+1) |
| 524 |  |  |  |  | 313 | |

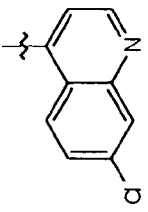
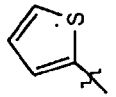

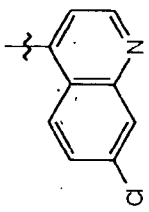
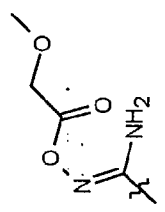

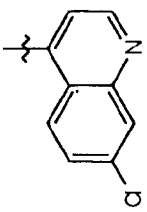

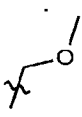
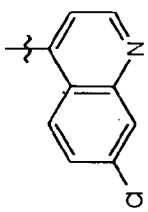
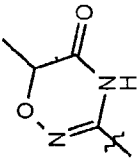

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 525 |  |  |  |  | 373 | |
| 526 |  |  |  |  | 386 | 387 (M+1) |
| 527 |  |  |  |  | 358 | 359 (M+1) |
| 528 |  |  |  |  | 428 | 429 (M+1) |

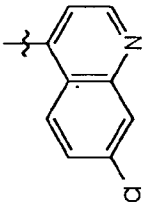


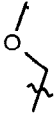
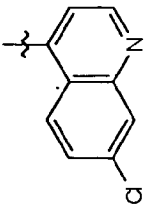

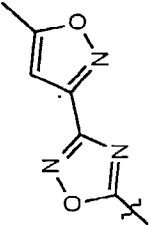

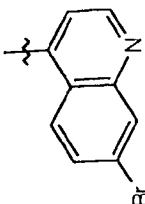

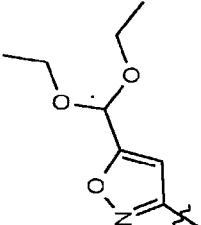
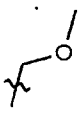
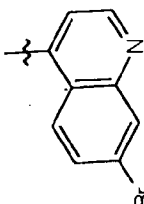

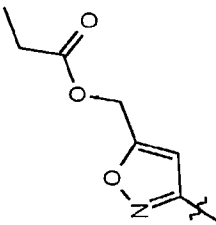
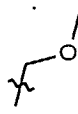
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|-----------------|----------------|
| 529 |  |  |  |  | 456 | 457 (M+1) |
| 530 |  |  |  |  | 498 | 499 (M+1) |
| 531 |  |  |  |  | 368 | 369 (M+1) |
| 532 |  |  |  |  | 438 | 439 (M+1) |

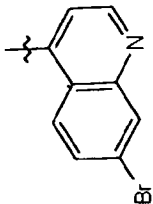

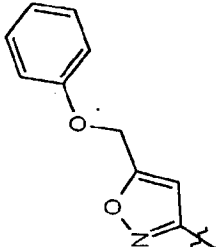
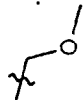
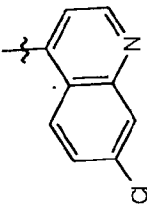

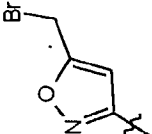
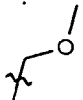
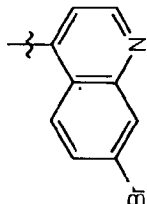

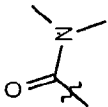

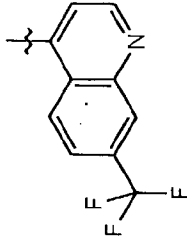

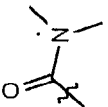

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 533 |  |  |  |  | 406 | 407 (M+1) |
| 534 |  |  |  |  | 412 | 413 (M+1) |
| 535 |  |  |  |  | 454 | 455 (M+1) |
| 536 |  |  |  |  | 426 | 427 (M+1) |

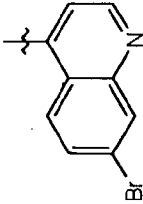
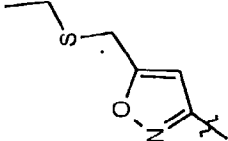
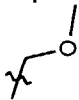
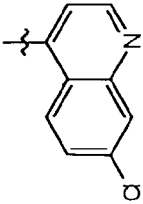
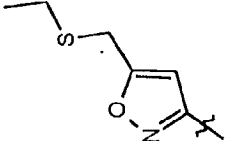
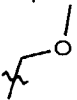
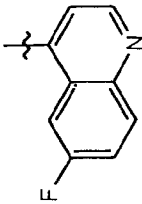
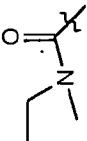

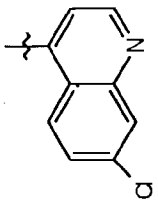
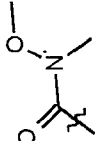

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|-----------------|----------------|
| 537 |  |  |  |  | 446 | 447 (M+1) |
| 538 |  |  |  |  | 407 | 408 (M+1) |
| 539 |  |  |  |  | 467 | 468 (M+1) |

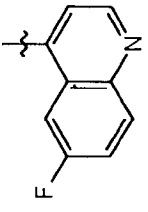



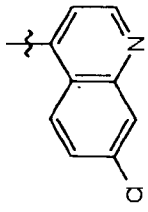

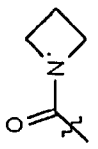

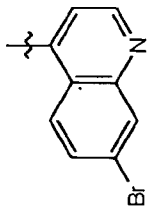

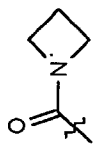

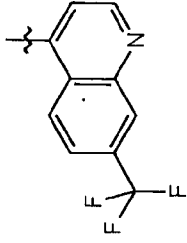

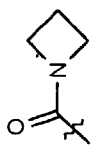

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 540 |  |  |  |  | 442 | 443 (M+1) |
| 541 |  |  |  |  | 328 | |
| 542 |  |  |  |  | 340 | |
| 543 |  |  |  |  | 340 | |

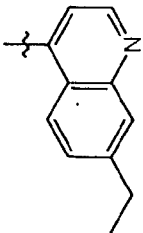

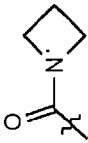

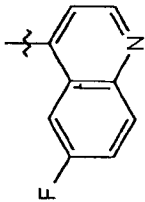

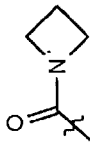

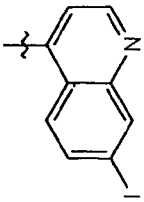

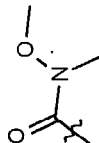

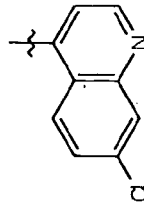

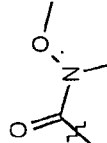

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|----------------------------------|---|---|-----------------|----------------|
| 544 |  | $\text{---} \text{H} \text{---}$ |  |  | 355 | 356 (M+1) |
| 545 |  | $\text{---} \text{H} \text{---}$ |  |  | 403 | |
| 546 |  | $\text{---} \text{H} \text{---}$ |  |  | 358 | 359 (M+1) |
| 547 |  | $\text{---} \text{H} \text{---}$ |  |  | 385 | 386 (M+1) |

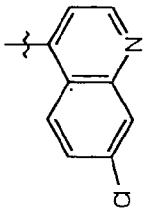

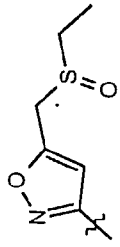

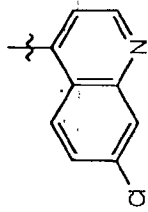

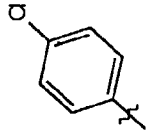

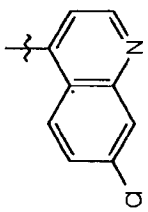

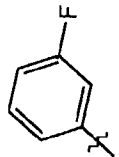

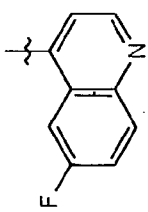



| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 548 |  |  |  |  | 344 | |
| 549 |  |  |  |  | 422 | 423 (M+1) |
| 550 |  |  |  |  | 486 | 487 (M+1) |
| 551 |  |  |  |  | 470 | 471 (M+1) |

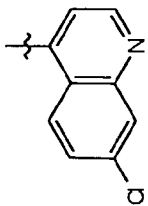

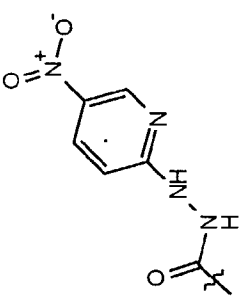

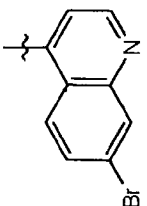

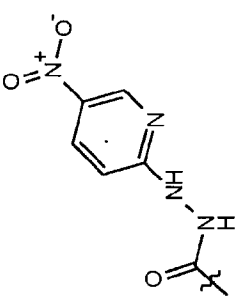

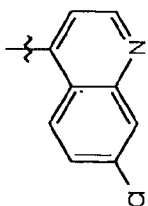

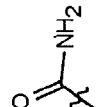

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 552 |  |  |  |  | 491 (M+1) | 490 |
| 553 |  |  |  |  | 433 (M+1) | 432 |
| 554 |  |  |  |  | 390 (M+1) | 388 |
| 555 |  |  |  |  | 380 (M+1) | 378 |

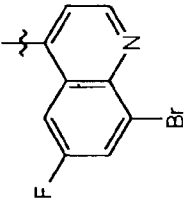

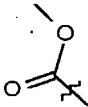

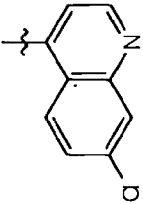

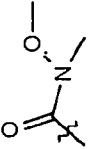
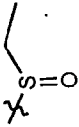
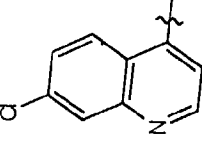

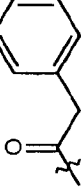
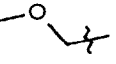
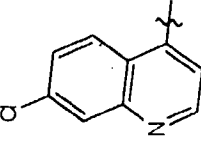

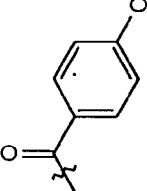
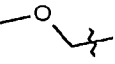
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---------------|---|---|-----------------|----------------|
| 556 |  | ---H |  |  | 458 | 460 (M+1) |
| 557 |  | ---H |  |  | 414 | 415 (M+1) |
| 558 |  | ---H |  |  | 342 | 343 (M+1) |
| 559 |  | ---H |  |  | 362 | 363 (M+1) |

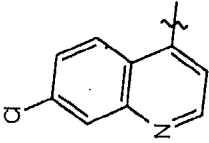

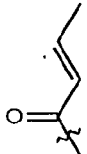
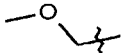
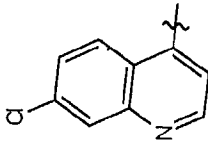

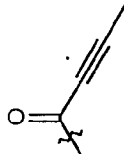
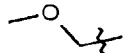
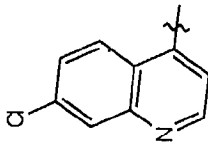

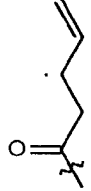
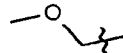
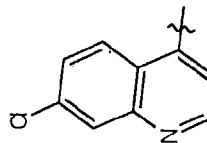

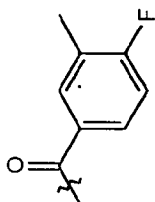
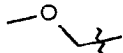
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 560 |  |  |  |  | 368 | 369 (M+1) |
| 561 |  |  |  |  | 356 | 357 (M+1) |
| 562 |  |  |  |  | 400 | 402 (M+1) |
| 563 |  |  |  |  | 390 | 391 (M+1) |

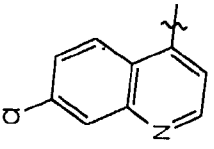

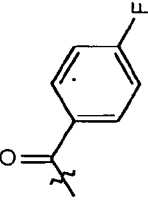
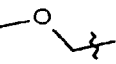
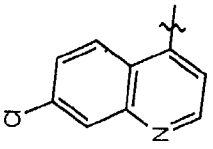

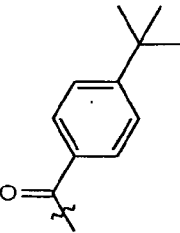
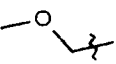
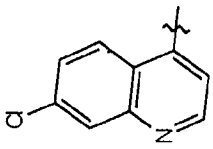

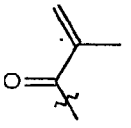
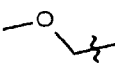
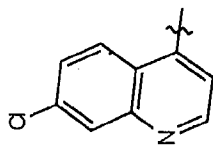

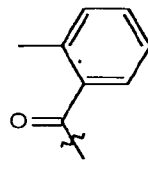
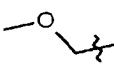
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 564 |  |  |  |  | 350 | 351 (M+1) |
| 565 |  |  |  |  | 340 | 341 (M+1) |
| 566 |  |  |  |  | 452 | 453 (M+1) |
| 567 |  |  |  |  | 378 | 379 (M+1) |

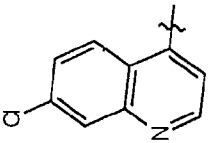


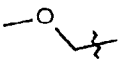
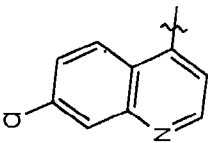

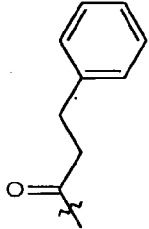
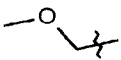
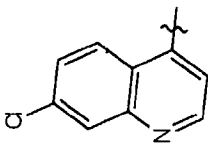

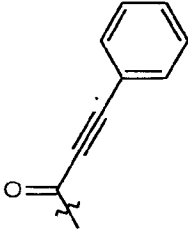
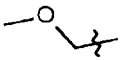
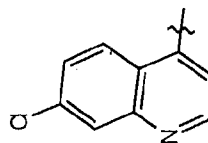

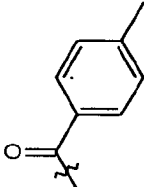
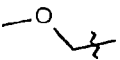
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 568 |  |  |  |  | 430 | 431 (M+1) |
| 569 |  |  |  |  | 383 | 384 (M+1) |
| 570 |  |  |  |  | 367 | 368 (M+1) |
| 571 |  |  |  |  | 335 | 337 (M+1) |

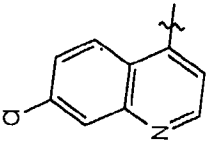

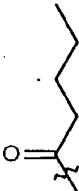
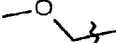
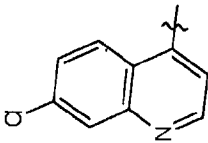

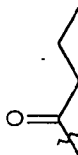

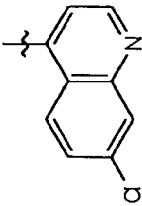

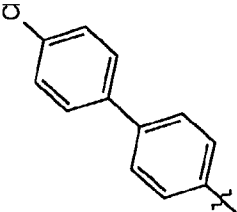

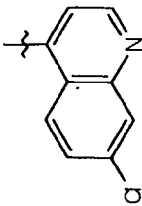

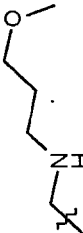

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|--|--|--|-----------------|----------------|
| 572 |  |  |  |  | 453 | 454 (M+1) |
| 573 |  |  |  |  | 497 | 498 (M+1) |
| 574 |  |  |  |  | 287 | 288 (M+1) |

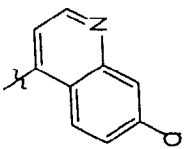
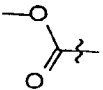
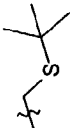
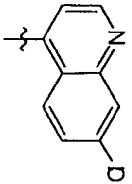


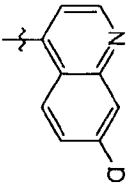
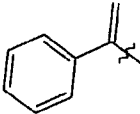

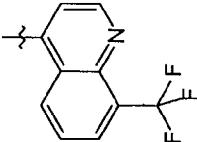


| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 575 |  |  |  |  | 393 | |
| 576 |  |  |  |  | 392 | 393 (M+1) |
| 577 |  |  |  |  | 391 | 392 (M+1) |
| 578 |  |  |  |  | 411 | 412 (M+1) |

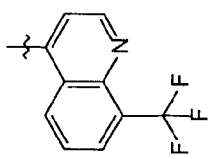

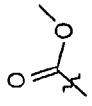

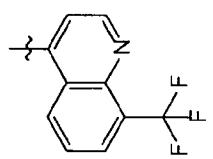

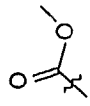

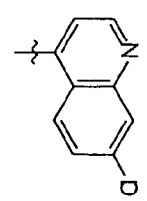

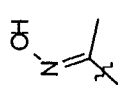
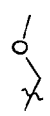
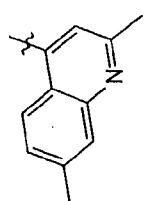

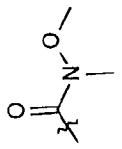
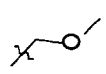
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 579 |  |  |  |  | 341 | 342 (M+1) |
| 580 |  |  |  |  | 339 | 340 (M+1) |
| 581 |  |  |  |  | 355 | 356 (M+1) |
| 582 |  |  |  |  | 409 | 410 (M+1) |

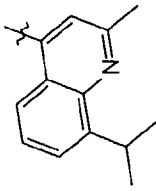
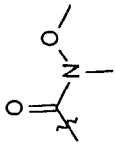

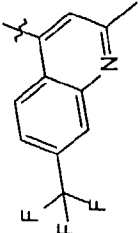
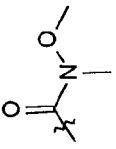
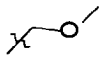
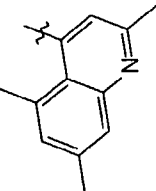
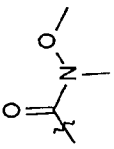

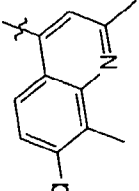
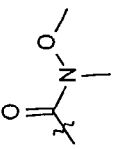

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 583 |  |  |  |  | 395 | 396 (M+1) |
| 584 |  |  |  |  | 433 | 434 (M+1) |
| 585 |  |  |  |  | 341 | 342 (M+1) |
| 586 |  |  |  |  | 391 | 392 (M+1) |

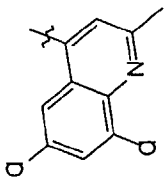

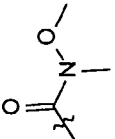

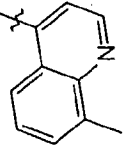

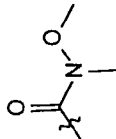
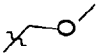
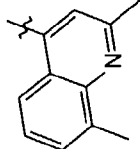

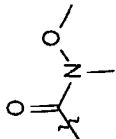

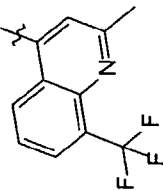

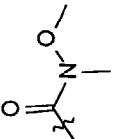

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 587 |  |  |  |  | 371 | 372 (M+1) |
| 588 |  |  |  |  | 405 | 404 (M-1) |
| 589 |  |  |  |  | 401 | 402 (M+1) |
| 590 |  |  |  |  | 391 | 392 (M+1) |

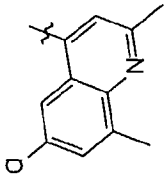

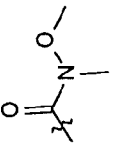

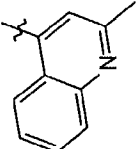

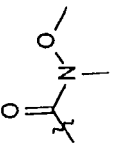

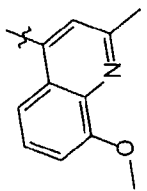

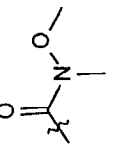

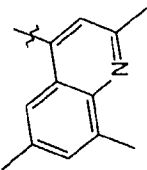

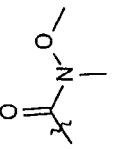

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 591 |  |  |  |  | 357 | 358 (M+1) |
| 592 |  |  |  |  | 343 | 344 (M+1) |
| 593 |  |  |  |  | 459 | 460 (M+1) |
| 594 |  |  |  |  | 374 | 375 (M+1) |

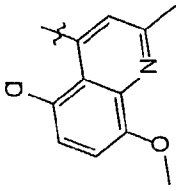

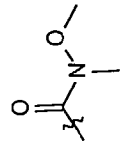

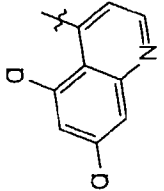

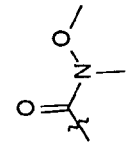

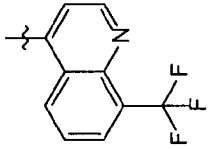

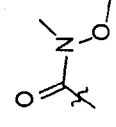

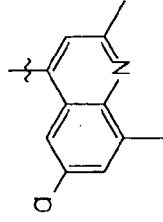

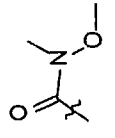
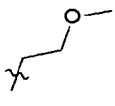
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 595 |  | ---H |  |  | 389 | 390 (M+1) |
| 596 |  | ---H |  |  | 301 | 302 (M+1) |
| 597 |  | ---H |  |  | 375 | |
| 598 |  |  |  | ---H | 349 | 350 (M+1) |

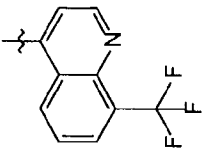

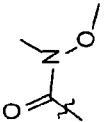
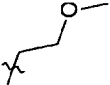
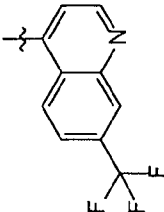

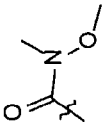
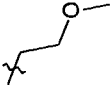
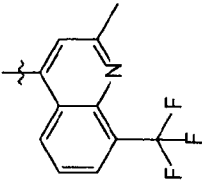

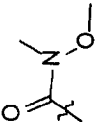

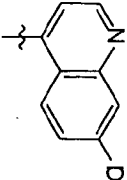

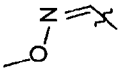

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 599 |  |  |  |  | 411 | 412 (M+1) |
| 600 |  |  |  |  | 399 | 400 (M+1) |
| 601 |  |  |  |  | 330 | |
| 602 |  |  |  |  | 354 | 355 (M+1) |

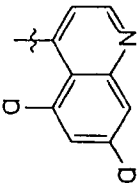
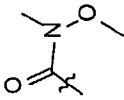

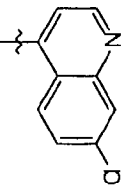

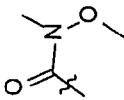
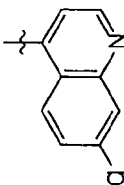

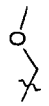
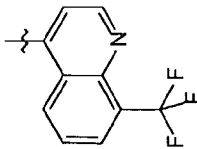

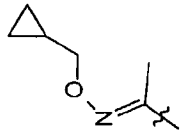
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---------------|---|---|-----------------|----------------|
| 603 |  | ---H |  |  | 382 | 383 (M+1) |
| 604 |  | ---H |  |  | 408 | 409 (M+1) |
| 605 |  | ---H |  |  | 368 | 369 (M+1) |
| 606 |  | ---H |  |  | 388 | 389 (M+1) |

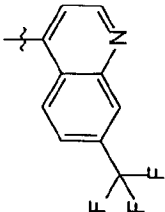

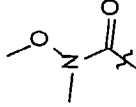

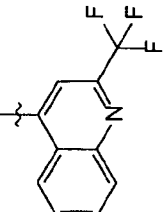

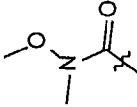

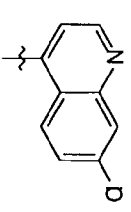

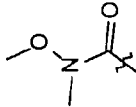

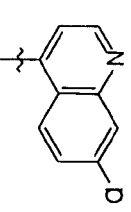

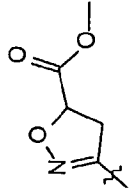

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 607 |  |  |  |  | 408 | 409 (M+1) |
| 608 |  |  |  |  | 340 | 341 (M+1) |
| 609 |  |  |  |  | 354 | 355 (M+1) |
| 610 |  |  |  |  | 408 | 409 (M+1) |

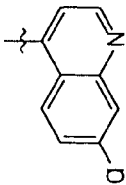

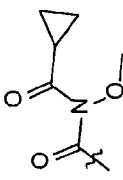
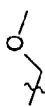
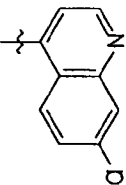

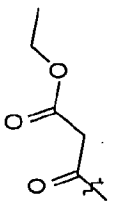

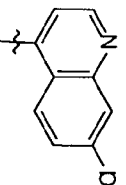

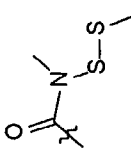
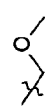
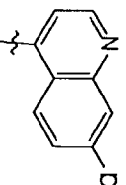

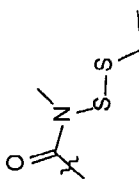
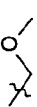
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 611 |  |  |  |  | 388 | 389 (M+1) |
| 612 |  |  |  |  | 340 | 341 (M+1) |
| 613 |  |  |  |  | 370 | 371 (M+1) |
| 614 |  |  |  |  | 368 | 369 (M+1) |

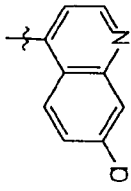
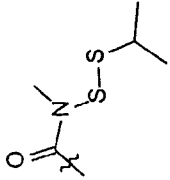
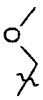
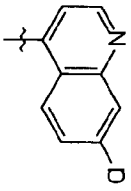
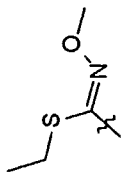

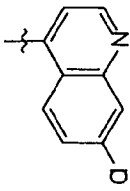
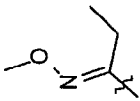
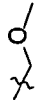
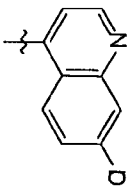
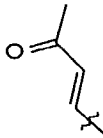

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 615 |  |  |  |  | 404 | 405 (M+1) |
| 616 |  |  |  |  | 394 | 395 (M+1) |
| 617 |  |  |  |  | 380 | |
| 618 |  |  |  |  | 402 | 403 (M+1) |

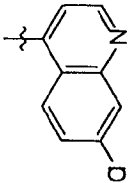
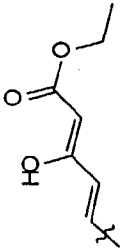

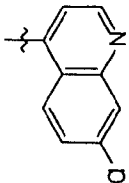
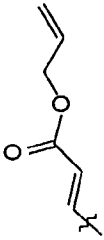

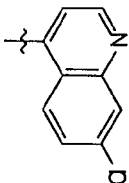
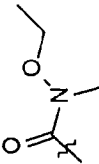

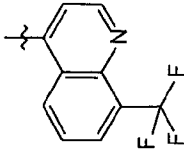

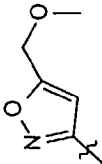
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 619 |  |  |  |  | 408 | 409 (M+1) |
| 620 |  |  |  |  | 408 | 409 (M+1) |
| 621 |  |  |  |  | 378 | 379 (M+1) |
| 622 |  |  |  |  | 330 | 331 (M+1) |

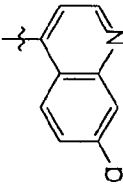

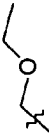

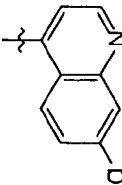

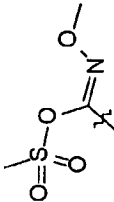

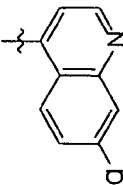

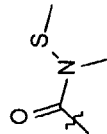

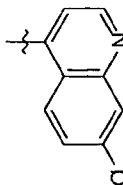

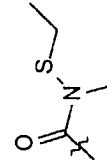

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|-----------------|----------------|
| 623 |  | ---H |  |  | 442 | 443 (M+1) |
| 624 |  |  |  | ---H | 486 | 487 (M+1) |
| 625 |  | ---H |  |  | 317 | 318 (M+1) |
| 626 |  |  |  | ---H | 418 | 418 (M+2) |

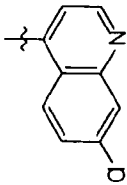

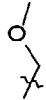
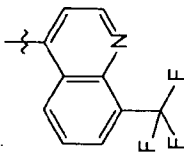


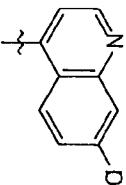
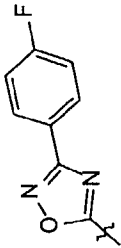
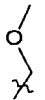
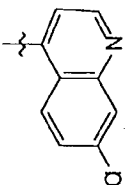
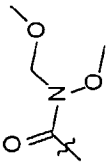

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 627 |  |  |  |  | 394 | 395 (M+1) |
| 628 |  |  |  |  | 394 | 395 (M+1) |
| 629 |  |  |  |  | 360 | 361 (M+1) |
| 630 |  |  |  |  | 400 | 401 (M+1) |

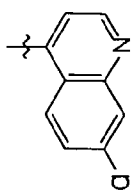

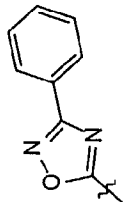
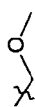
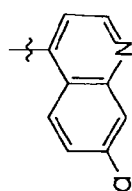

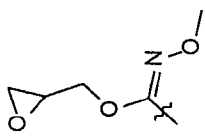

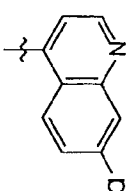

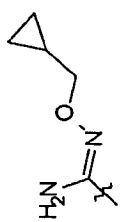
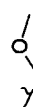
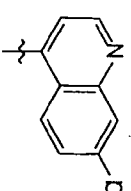

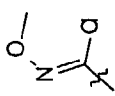
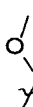
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|-----------------|----------------|
| 631 |  |  |  |  | 414 | |
| 632 |  |  |  |  | 387 | 388 (M+1) |
| 633 |  |  |  |  | 408 | 409 (M+1) |
| 634 |  |  |  |  | 422 | 423 (M+1) |

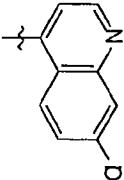
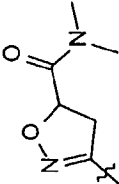

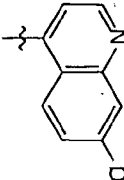
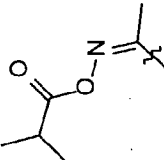

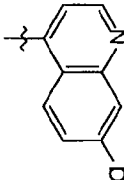
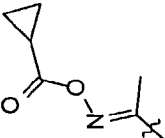

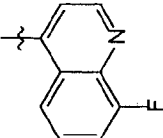

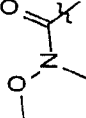
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---------------------------------|---|---|-----------------|----------------|
| 635 |  | $\text{---}\text{CH}\text{---}$ |  |  | 436 | |
| 636 |  | $\text{---}\text{CH}\text{---}$ |  |  | 390 | |
| 637 |  | $\text{---}\text{CH}\text{---}$ |  |  | 358 | |
| 638 |  | $\text{---}\text{CH}\text{---}$ |  |  | 341 | |

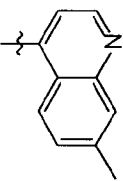

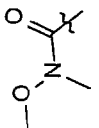

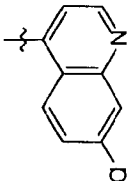

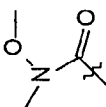
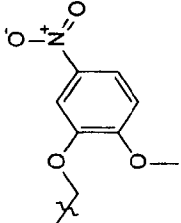
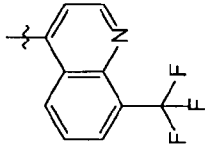

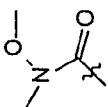
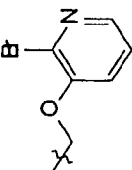
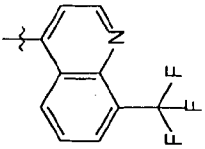

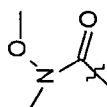
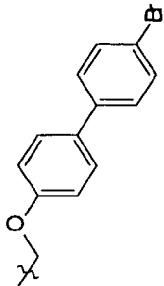
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|-----------------|----------------|
| 639 |  | ---H |  |  | 413 | |
| 640 |  | ---H |  |  | 383 | |
| 641 |  | ---H |  |  | 374 | |
| 642 |  |  |  | ---H | 418 | 419 (M+1) |

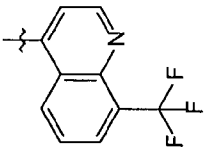
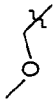
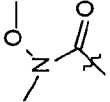

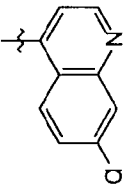

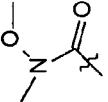
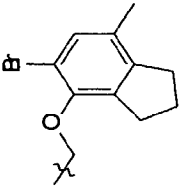
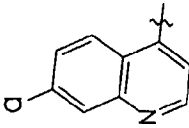

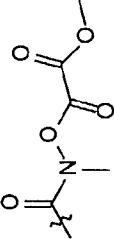
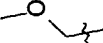
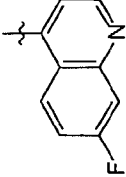

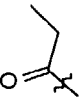

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|-----------------|----------------|
| 643 |  |  |  |  | 331 | 332 (M+1) |
| 644 |  |  |  |  | 424 | 425 (M+1) |
| 645 |  |  |  |  | 376 | 377 (M+1) |
| 646 |  |  |  |  | 390 | 391 (M+1) |

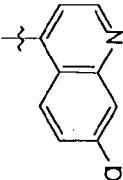

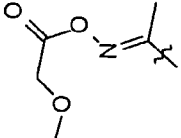

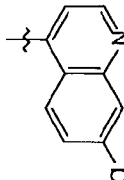

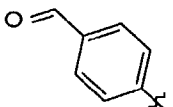

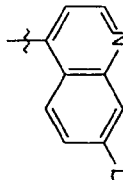

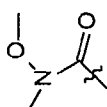
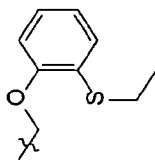
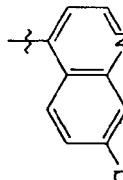

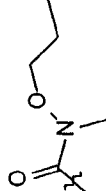

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 647 |  | ---H |  |  | 312 | 313 (M+1) |
| 648 |  |  |  | ---H | 364 | 365 (M+1) |
| 649 |  | ---H |  |  | 435 | 436 (M+1) |
| 650 |  | ---H |  |  | 390 | 391 (M+1) |

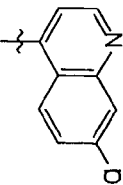

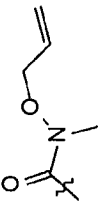

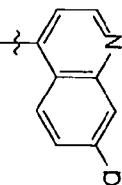

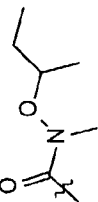

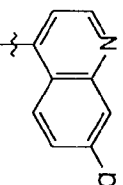

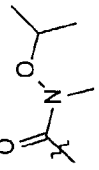

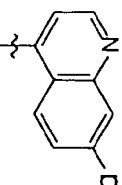

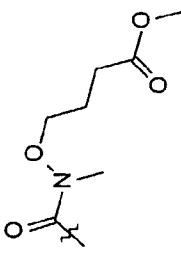

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 651 |  |  |  |  | 417 | 418 (M+1) |
| 652 |  |  |  |  | 402 | 403 (M+1) |
| 653 |  |  |  |  | 385 | 386 (M+1) |
| 654 |  |  |  |  | 364 | 365 (M+1) |

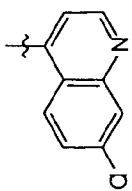

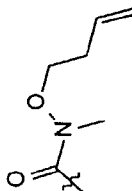

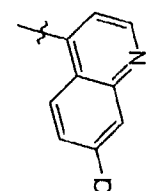

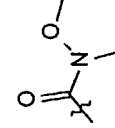
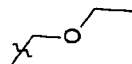
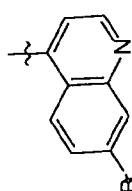

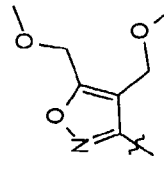

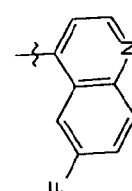

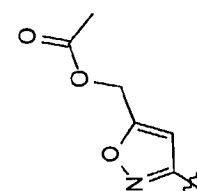

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 655 |  | ---H |  |  | 413 | |
| 656 |  | ---H |  |  | 400 | |
| 657 |  | ---H |  |  | 398 | |
| 658 |  |  |  | ---H | 344 | 345 (M+1) |

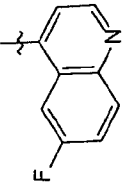
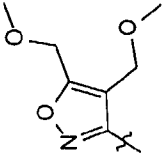

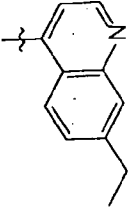
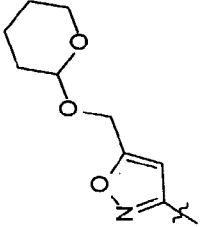

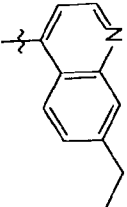
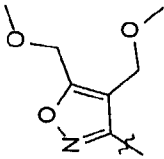

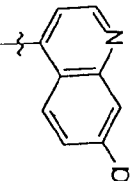
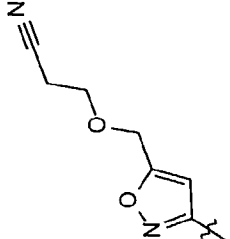

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 659 |  |  |  |  | 340 | 341 (M+1) |
| 660 |  |  |  |  | 497 | 498 (M+1) |
| 661 |  |  |  |  | 535 | 536 (M+1) |
| 662 |  |  |  |  | 610 | 611 (M+1) |

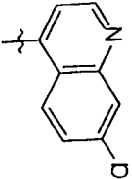
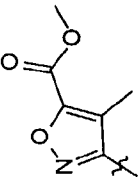

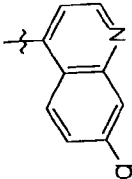
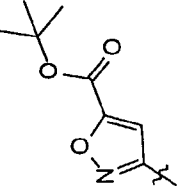

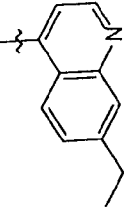
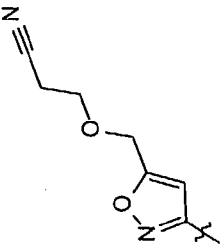

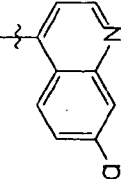
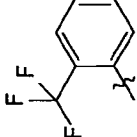

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 663 |  |  |  |  | 428 | 429 (M+1) |
| 664 |  |  |  |  | 554 | 555 (M+1) |
| 665 |  |  |  |  | 432 | 433 (M+1) |
| 666 |  |  |  |  | 313 | |

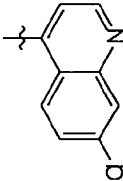
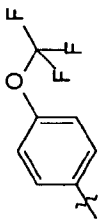

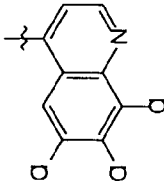


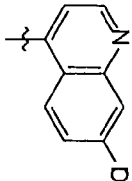
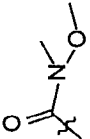
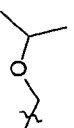
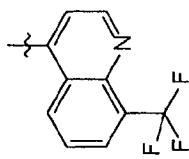



| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 667 |  |  |  |  | 402 | |
| 668 |  |  |  |  | 377 | 378 (M+1) |
| 669 |  |  |  |  | 482 | 483 (M+1) |
| 670 |  |  |  |  | 388 | 389 (M+1) |

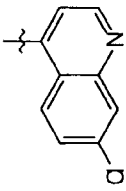

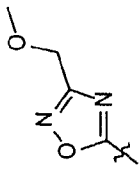

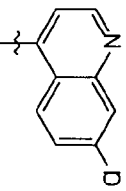

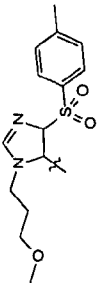

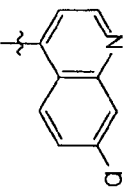


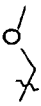
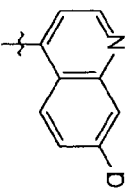



| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|--|---|-----------------|----------------|
| 671 |  |  |  |  | 386 | 387 (M+1) |
| 672 |  |  |  |  | 402 | 403 (M+1) |
| 673 |  |  |  |  | 388 | 389 (M+1) |
| 674 |  |  |  |  | 446 | 447 (M+1) |

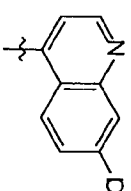

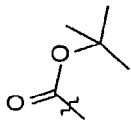

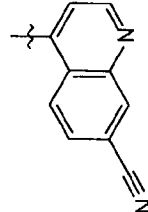

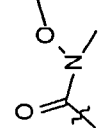
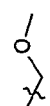
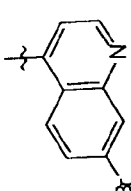

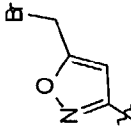

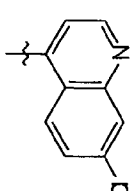

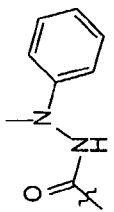
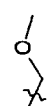
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 675 |  |  |  |  | 400 | 401 (M+1) |
| 676 |  |  |  |  | 374 | 375 (M+1) |
| 677 |  |  |  |  | 472 | 473 (M+1) |
| 678 |  |  |  |  | 396 | 397 (M+1) |

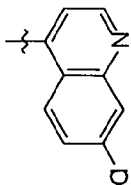

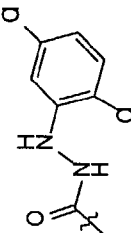

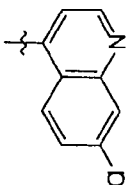

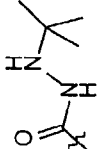

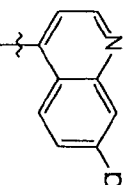

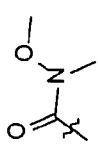
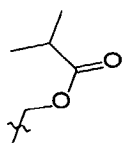
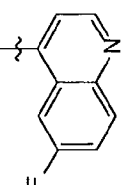

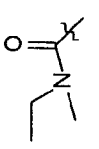

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---------------|---|---|-----------------|----------------|
| 679 |  | ---H |  |  | 412 | 413 (M+1) |
| 680 |  | ---H |  |  | 448 | 449 (M+1) |
| 681 |  | ---H |  |  | 422 | 423 (M+1) |
| 682 |  | ---H |  |  | 423 | 424 (M+1) |

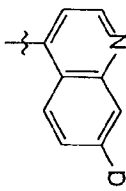

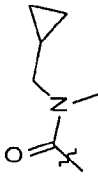

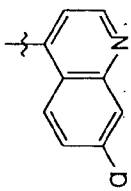

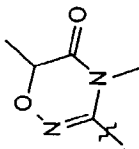
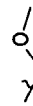
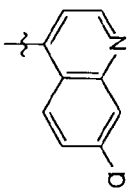

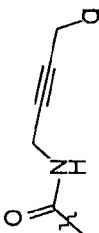

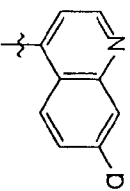

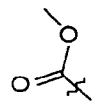

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---------------|---|---|-----------------|----------------|
| 683 |  | ---H |  |  | 412 | |
| 684 |  | ---H |  |  | 440 | 441 (M+1) |
| 685 |  | ---H |  |  | 417 | 418 (M+1) |
| 686 |  | ---H |  |  | 417 | 418 (M+1) |

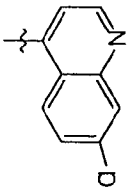
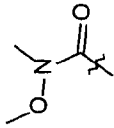

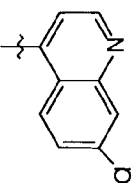
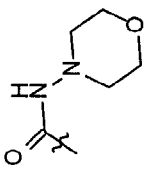

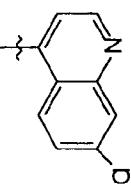
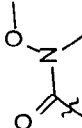

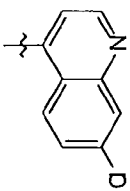
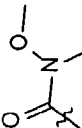
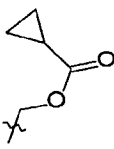
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 687 |  | $\text{--}\dot{\text{C}}\text{H--}$ |  |  | 433 | 434 (M+1) |
| 688 |  | $\text{--}\dot{\text{C}}\text{H--}$ |  |  | 399 | |
| 689 |  | $\text{--}\dot{\text{C}}\text{H--}$ |  |  | 388 | |
| 690 |  |  |  |  | 447 | 448 (M+1) |

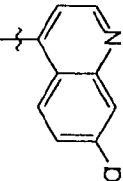

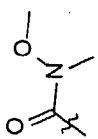
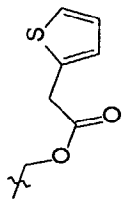
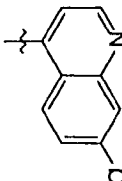



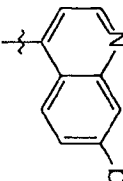

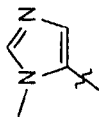

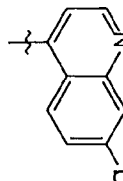

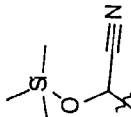

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|---|---|-----------------|----------------|
| 691 |  |  |  |  | 385 | |
| 692 |  |  |  |  | 567 | 568 (M+1) |
| 693 |  |  |  |  | 356 | 357 (M+1) |
| 694 |  |  |  |  | 358 | 359 (M+1) |

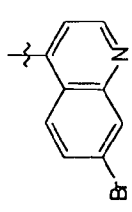

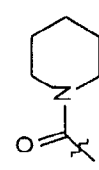
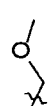
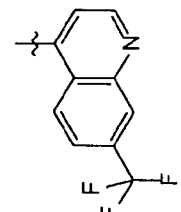

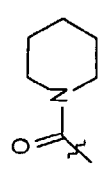
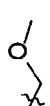
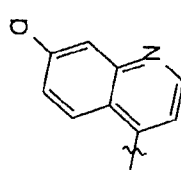



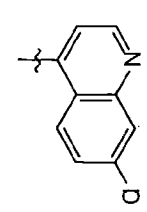

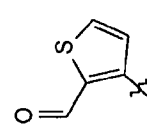
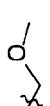
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 695 |  |  |  |  | 373 | 374 (M+1) |
| 696 |  |  |  |  | 351 | 352 (M+1) |
| 697 |  |  |  |  | 476 | 477 (M+1) |
| 698 |  |  |  |  | 421 | 422 (M+1) |

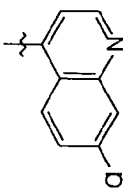
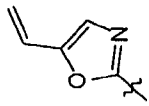

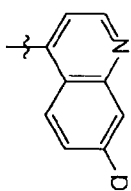
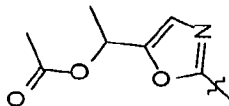
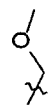
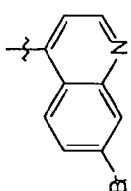
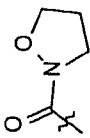

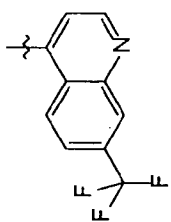
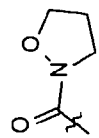

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 699 |  |  |  |  | 475 | 476 (M+1) |
| 700 |  |  |  |  | 387 | 388 (M+1) |
| 701 |  |  |  |  | 416 | 417 (M+1) |
| 702 |  |  |  |  | 342 | 343 (M+1) |

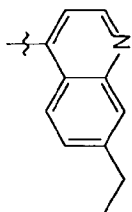

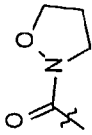

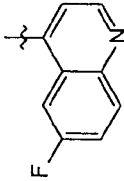

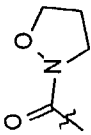

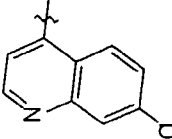

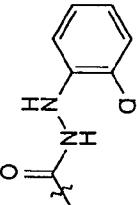
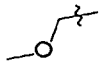
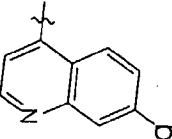

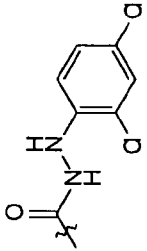

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 703 |  |  |  |  | 384 | 385 (M+1) |
| 704 |  |  |  |  | 399 | 400 (M+1) |
| 705 |  |  |  |  | 402 | 403 (M+1) |
| 706 |  |  |  |  | 317 | 318 (M+1) |

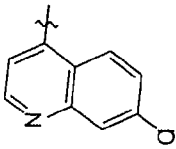

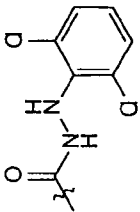

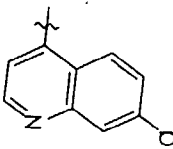

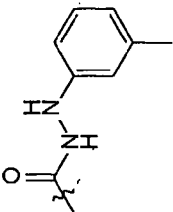

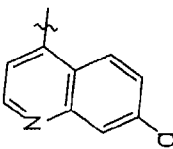

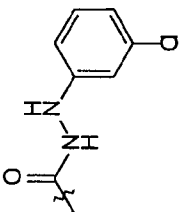

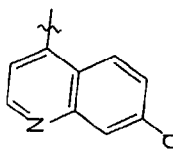

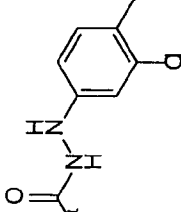

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|----------------------|---|---|-----------------|----------------|
| 707 |  | $\text{---}\text{H}$ |  |  | 376 | 377 (M+1) |
| 708 |  | $\text{---}\text{H}$ |  |  | 401 | 402 (M+1) |
| 709 |  | $\text{---}\text{H}$ |  |  | 362 | 363 (M+1) |
| 710 |  | $\text{---}\text{H}$ |  |  | 414 | |

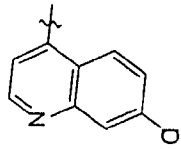

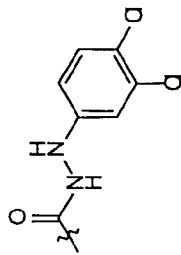

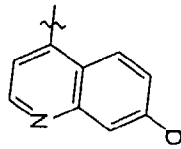

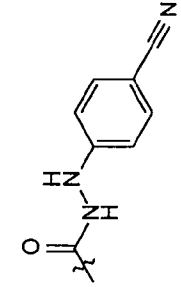

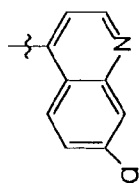

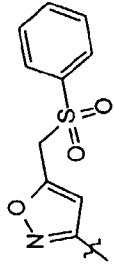

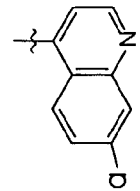

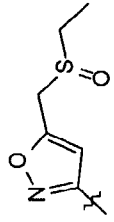
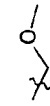
| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|--|---|--|---|-----------------|----------------|
| 711 |  |  |  |  | 470 | 471 (M+1) |
| 712 |  |  |  |  | 411 | 412 (M+1) |
| 713 |  |  |  |  | 353 | 354 (M+1) |
| 714 |  |  |  |  | 400 | 401 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 715 |  |  |  |  | 428 | 430 (M+1) |
| 716 |  |  |  |  | 418 | 419 (M+1) |
| 717 |  |  |  |  | 269 | |
| 718 |  |  |  |  | 383 | 384 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---------------|---|---|-----------------|----------------|
| 719 |  | ---H |  |  | 366 | 367 (M+1) |
| 720 |  | ---H |  |  | 426 | 427 (M+1) |
| 721 |  | ---H |  |  | 416 | |
| 722 |  | ---H |  |  | 406 | |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 723 |  |  |  |  | 366 | |
| 724 |  |  |  |  | 356 | 357 (M+1) |
| 725 |  |  |  |  | 441 | 442 (M+1) |
| 726 |  |  |  |  | 475 | 476 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 727 |  |  |  |  | 475 | 476 (M+1) |
| 728 |  |  |  |  | 421 | 422 (M+1) |
| 729 |  |  |  |  | 441 | 442 (M+1) |
| 730 |  |  |  |  | 455 | 456 (M+1) |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 731 |  |  |  |  | 475 | 476 (M+1) |
| 732 |  |  |  |  | 432 | 433 (M+1) |
| 733 |  |  |  |  | 494 | 495 (M+1) |
| 734 |  |  |  |  | 430 | |

| n° | A | B | C | D | Masse théorique | Masse observée |
|-----|---|---|---|---|-----------------|----------------|
| 735 | | | | | 383 | 384 (M+1) |
| 736 | | | | | 401 | 402 (M+1) |
| 737 | | | | | 374 | 375 (M+1) |
| 738 | | | | | 451 | |

[0058] Les modes opératoires présentés ci-dessous illustrent des procédés de préparation de quelques uns de ces composés.

Il est bien entendu que les procédés qui suivent sont directement transposables à la synthèse de l'ensemble des composés de la présente invention.

5 De plus d'autres voies de synthèse, aisément accessibles à l'homme du métier, peuvent être mises en œuvre pour accéder aux composés de l'invention.

Exemple 1 : Préparation du composé n° 11

Préparation du 3-(méthoxyméthyl)-1-[8-(trifluorométhyl)-4-quinolyl]-1H-pyrazole-
10 4-carboxylate de méthyle.

Etape 1 :

On dissout 50g de 4-méthoxy-3-oxobutanoate de méthyle dans 500 ml de toluène puis on ajoute 77,3 g de N,N-diméthylformamide diméthylacétal et on chauffe à 90° C pendant 5 heures tout en distillant au moyen d'un Dean-Stark le méthanol qui se
15 forme. On évapore ensuite le milieu réactionnel sous vide et on utilise le 3-(diméthylamino)-2(2-méthoxyacétyl)-2-propénoate de méthyle brut obtenu tel quel par la suite.

Etape 2 :

On dissout 40 g de 3-(diméthylamino)-2(2-méthoxyacétyl)-2-propénoate de méthyle
20 dans 100 ml d'acide acétique et on additionne doucement 9,6 ml d'hydrazine. On chauffe ensuite pendant 3 heures à 90°C. On laisse revenir à température ambiante, ajoute 1l d'eau et on neutralise l'acide acétique en versant doucement du bicarbonate de potassium jusqu'à la fin du dégagement gazeux. On extrait ensuite avec de l'acétate d'éthyle, lave la phase organique avec de l'eau. On la sèche ensuite sur du
25 sulfate de magnésium et l'évapore pour obtenir 28,7g de 5-(méthoxyméthyl)-1H-pyrazole-4-carboxylate de méthyle sous la forme d'un solide marron que l'on utilise tel quel par la suite.

Etape 3 :

On dissout 5,7 g de 5-(méthoxyméthyl)-1H-pyrazole-4-carboxylate de méthyle dans
30 60ml de diméthylformamide et l'on ajoute 17 ml d'une solution 2M de 1-terbutyl-2,2,4,4,4-pentakis-(diméthylamino)-2λ⁵,4λ⁵-caténadi(phosphazène) dans le tétrahydrofurane. On agite pendant 10 minutes la solution puis on ajoute 7,74g de 4-chloro-8-trifluorométhylquinoléine et on chauffe pendant 4 heures à 70°C. On laisse ensuite revenir le mélange réactionnel à température ambiante, extrait avec de
35 l'acétate d'éthyle, lave la phase organique avec une solution saturée de chlorure de lithium puis avec de l'eau. On sèche la phase organique sur du sulfate de magnésium, l'évapore et le produit brut obtenu est purifié par chromatographie flash avec

successivement 15 puis 30 puis 40% d'acétate d'éthyle dans l'heptane pour obtenir 8g d'un solide beige. Ce produit peut-être recristallisé dans du diisopropyléther pour obtenir du 3-(méthoxyméthyl)-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazole-4-carboxylate de méthyle sous la forme d'un solide blanc.

5 F = 138°C (on désigne par cette expression le point de fusion)

Exemple 2 : Préparation du composé n° 6

Préparation de 1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle

10 On dissout 15 g de 3-(diméthylamino)-2(2-méthoxyacétyl)-2-propénoate de méthyle dans 100 ml d'acide acétique et on ajoute 14,4g de 7-chloro-4-hydrazinoquinoléine et on chauffe à 90°C. Au bout d'une heure on laisse revenir à température ambiante et on ajoute 100 ml supplémentaire d'acide acétique. On chauffe encore pendant 3 heures à 90°C puis on laisse revenir à température ambiante, verse sur 1l d'eau puis
15 filtre le précipité marron qui se forme. On ajoute de l'heptane sur le précipité, évapore les solvants et l'on obtient 15,7 g d'un solide beige.

F = 123°C.

Exemple 3 : Préparation du composé n° 61

20 Préparation de 1-(7-chloro-4-quinolyl)-*N,N*-diéthyl-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxamide

À une suspension de 6,6ml de *N,N*-diéthylamine dans 70 ml de 1,2-dichloroéthane, on ajoute doucement 425 ml d'une solution 2M de triméthylaluminium dans l'hexane à 0°C puis on agite à température ambiante pendant 20 minutes. On ajoute ensuite 7g
25 de 1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle et on chauffe le mélange réactionnel à 75°C pendant 20 heures. On refroidit le mélange à 0°C et hydrolyse doucement avec une solution d'acide chlorhydrique 1 molaire jusqu'à la fin du dégagement gazeux et l'on extrait au dichlorométhane. Après séchage et évaporation de la phase organique on obtient 6,84g d'une huile
30 brune qui est purifiée par chromatographie flash avec un éluant 70/30 acétate d'éthyle/heptane puis 100% acétate d'éthyle pour obtenir 3,1g d'un solide brun.

F = 114°C.

Exemples d'activités biologiques des composés de l'invention

35

Exemple A : Test *in vivo* sur *Septoria nodorum* (septoriose du blé) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- eau,
- agent tensioactif Tween 80 (oléate de dérivé polyoxyéthyléné du sorbitan) dilué à 10% dans l'eau : 5 ml/mg de matière active,
- argile : support inerte qsp 100%.

Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

- 10 Des plants de blé (variété Scipion) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont traités au stade 1 feuille (10 cm de hauteur) par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins, sont traités par une solution aqueuse ne contenant pas la matière active.

- 15 Après 24 heures, les plants sont contaminés par pulvérisation d'une suspension aqueuse de spores (500 000 spores par cm³) de *Septoria nodorum*. Les spores sont récoltées sur une culture âgée de sept jours.

Les plants de blé contaminés sont mis en incubation pendant 72 heures à 18°C environ, en atmosphère humide, puis pendant 14 jours à 90 % d'humidité relative.

- 20 La notation est effectuée 15 à 20 jours après la contamination, en comparaison avec les plants témoins.

Dans ces conditions, on observe, à la dose de 500 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples 11, 135, 136, 287, et 387.

25

Exemple B : Test *in vivo* sur *Erysiphe graminis* f. sp. *tritici* (oïdium du blé) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- 30
- eau
 - agent tensioactif Tween 80 (oléate de dérivé polyoxyéthyléné du sorbitan) dilué à 10% dans l'eau : 5 ml/mg de matière active
 - argile : support inerte qsp 100%.

- 35 Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

Des plants de blé (variété Audace) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont traités au stade 1 feuille (10 cm de

hauteur) par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

Après 24 heures, les plants sont contaminés par saupoudrage avec des spores
5 d'*Erisyphe graminis* f. sp. *tritici*, le saupoudrage étant effectué à l'aide de plants malades.

La notation est effectuée 7 à 14 jours après la contamination, en comparaison avec les plants témoins.

Dans ces conditions, on observe à la dose de 500 g/ha, une protection bonne (au
10 moins 50%) ou totale avec les composés décrits dans les exemples 6, 11, 61, 67, 136, 163, 170, 215, 217 et 430.

Exemple C : Test *in vivo* sur *Erisyphe graminis* f. sp. *hordei* (oïdium de l'orge) :

15 Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- eau

- agent tensioactif Tween 80 (oléate de dérivé polyoxyéthyléné du sorbitan) dilué à 10% dans l'eau : 5 ml/mg de matière active

20 - argile : support inerte qsp 100%.

Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

Des plants d'orge (variété Express) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont traités au stade 1 feuille (10 cm de
25 hauteur) par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

Après 24 heures, les plants sont contaminés par saupoudrage avec des spores
30 d'*Erisyphe graminis* f. sp. *hordei*, le saupoudrage étant effectué à l'aide de plants malades.

La notation est effectuée 7 à 14 jours après la contamination, en comparaison avec les plants témoins.

Dans ces conditions, on observe à la dose de 500 g/ha, une protection bonne (au
35 moins 50%) ou totale avec les composés décrits dans les exemples 11, 41, 61, 67, 91, 119, 163, 170, 215, 217, 306, 310 et 430.

Exemple D : Test *in vivo* sur *Puccinia recondita* (rouille brune du blé) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- eau

- 5 - agent tensioactif Tween 80 (oléate de dérivé polyoxyéthyléné du sorbitan) dilué à 10% dans l'eau : 5 ml/mg de matière active
- argile : support inerte qsp 100%.

Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

- 10 Des plants de blé (variété Scipion) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont traités au stade 1 feuille (10 cm de hauteur) par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

- 15 Après 24 heures, les plants sont contaminés par pulvérisation d'une suspension aqueuse de spores (100 000 spores par cm³) de *Puccinia recondita*. Les spores sont récoltées sur des plants malades.

Les plants de blé contaminés sont mis en incubation pendant 24 heures à 18°C environ, en atmosphère humide, puis pendant 7 à 14 jours à 60 % d'humidité relative.

- 20 La notation est effectuée 8 à 15 jours après la contamination, en comparaison avec les plants témoins.

Dans ces conditions, on observe à la dose de 500 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples 11, 88, 119, 136 et 155.

25

Exemple E : Test *in vivo* sur *Pyrenophora teres* (helminthosporiose de l'orge) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- 30 - eau

- agent tensioactif Tween 80 (oléate de dérivé polyoxyéthyléné du sorbitan) dilué à 10% dans l'eau : 5 ml/mg de matière active
- argile : support inerte qsp 100%.

- Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la
35 concentration désirée en matière active.

Des plants d'orge (variété Express) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont traités au stade 1 feuille (10 cm de

hauteur) par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

Après 24 heures, les plants sont contaminés par pulvérisation d'une suspension
5 aqueuse de spores (10 000 spores par cm³) de *Pyrenophora teres*. Les spores sont récoltées sur une culture âgée de 10 jours.

Les plants d'orge contaminés sont mis en incubation pendant 24 heures à 18°C environ, en atmosphère humide, puis pendant 7 à 14 jours à 80 % d'humidité relative. La notation est effectuée 8 à 15 jours après la contamination, en comparaison avec
10 les plants témoins.

Dans ces conditions, on observe à la dose de 500 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples 11, 41, 61, 119, 136, 155, 163, 170 et 430.

15 **Exemple F** : Test curatif *in vivo* sur *Erysiphe graminis* f. sp. *tritici* (oïdium du blé) :

Des plants de blé (variété Audace) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont contaminés au stade 1 feuille (10 cm de hauteur) par saupoudrage avec des spores d'*Erysiphe graminis* f. sp. *tritici*, le
20 saupoudrage étant effectué à l'aide de plants malades.

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- eau
- agent tensioactif Tween 80 (oléate de dérivé polyoxyéthyléné du sorbitan) dilué à
25 10% dans l'eau : 5 ml/mg de matière active
- argile : support inerte qsp 100%.

Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

Les plants de blé (variété Audace) contaminés, sont traités 48, 72 et 96 heures après
30 contamination par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

La notation est effectuée 7 à 14 jours après la contamination, en comparaison avec les plants témoins.

35 Dans ces conditions, on observe à la dose de 500 g/ha, une protection bonne (au moins 50%) ou totale avec le composé décrit dans l'exemple 67.

Exemple G : Test *in vivo* sur *Erysiphe graminis* f. sp. *tritici* (oïdium du blé) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- 5 - eau
- mélange spécifique à base de Soprophor BS4, de cyclohexanone, de N-méthylpyrrolidone et de N-octyl pyrrolidone à raison de 100 µl pour 10 mg de matière active. Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.
- 10 Des plants de blé (variété Audace) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont traités au stade 1 feuille (10 cm de hauteur) par pulvérisation de la suspension aqueuse décrite ci-dessus.
- Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.
- 15 Après 24 heures, les plants sont contaminés par saupoudrage avec des spores de *Erysiphe graminis* f. sp. *tritici* , le saupoudrage étant effectué à l'aide de plants malades.
- La notation est effectuée 7 à 14 jours après la contamination, en comparaison avec les plants témoins.
- 20 Dans ces conditions, on observe à la dose de 250 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples 31, 34, 41, 43, 53, 78, 93, 94, 101, 738.

Exemple H : Test *in vivo* sur *Erysiphe graminis* s f. sp. *hordei* (oïdium de l'orge) :

- 25 Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :
- eau
- mélange spécifique à base de Soprophor BS4, de cyclohexanone, de N-méthylpyrrolidone et de N-octyl pyrrolidone à raison de 100 µl pour 10 mg de matière active.
- 30 Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.
- Des plants d'orge (variété Express) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont traités au stade 1 feuille (10 cm de
- 35 hauteur) par pulvérisation de la suspension aqueuse décrite ci-dessus.
- Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.
- Après 24 heures, les plants sont contaminés par saupoudrage avec des spores de

Erysiphe graminis f. sp. *hordei* , le saupoudrage étant effectué à l'aide de plants malades.

La notation est effectuée 7 à 14 jours après la contamination, en comparaison avec les plants témoins.

- 5 Dans ces conditions, on observe à la dose de 250 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples 31, 34, 41, 43, 53, 78, 93, 94, 101, 738.

Exemple I : Test curatif *in vivo* sur *Erysiphe graminis* f. sp. *tritici* (oïdium du blé) :

10

Des plants de blé (variété Audace) en godets, semés sur un substrat tourbe terre-pouzzolane 50/50 et cultivés à 12°C, sont contaminés au stade 1 feuille (10 cm de hauteur) par saupoudrage avec des spores de *Erysiphe graminis* f. sp. *tritici* , le saupoudrage étant effectué à l'aide de plants malades.

- 15 Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- eau

- mélange spécifique à base de Soprophor BS4, de cyclohexanone, de N-méthyl pyrrolidone et de N-octyl pyrrolidone à raison de 100 µl pour 10 mg de matière active.

- 20 Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

Les plants de blé (variété Audace) contaminés, sont traités 48 heures après contamination par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

25

La notation est effectuée 7 à 14 jours après la contamination, en comparaison avec les plants témoins.

Dans ces conditions, on observe à la dose de 250 g/ha, une protection bonne (au moins 50%) ou totale avec le composé décrit dans les exemples 31, 34, 67.

30

Exemple J : Test *in vivo* sur *Uncinula necator* (oïdium de la vigne) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

35 - eau

- mélange spécifique à base de Soprophor BS4, de cyclohexanone, de N-méthyl pyrrolidone et de N-octyl pyrrolidone à raison de 100 µl pour 10 mg de matière active.

Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la

concentration désirée en matière active.

Des plants de vigne (variété Chardonnay) en godets sont traités au stade 5-6 feuilles (6 semaines après bouturage) par pulvérisation de la suspension aqueuse décrite ci-dessus.

- 5 Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

Après 24 heures, les plants sont contaminés par saupoudrage avec des spores de *Uncinula necator*, le saupoudrage étant effectué à l'aide de plants malades.

- 10 La notation est effectuée 30 jours après la contamination, en comparaison avec les plants témoins.

Dans ces conditions, on observe à la dose de 250 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples les exemples 31, 34, 43, 67.

- 15 **Exemple K** : Test *in vivo* sur *Sphaerotheca fuliginea* (oïdium des cucurbitacées) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est obtenue par broyage fin de celle-ci dans le mélange suivant :

- eau

- 20 - mélange spécifique à base de Soprophor BS4, de cyclohexanone, de N-méthyl pyrrolidone et de N-octyl pyrrolidone à raison de 100 µl pour 10 mg de matière active. Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

- 25 Des concombres (variété Marketer) en godets sont traités au stade 2 feuilles étalées par pulvérisation de la suspension aqueuse décrite ci-dessus.

Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant pas la matière active.

Après 24 heures, les plants sont contaminés par saupoudrage avec des spores *Sphaerotheca fuliginea*, le saupoudrage étant effectué à l'aide de plants malades.

- 30 La notation est effectuée 3 semaines après la contamination, en comparaison avec les plants témoins.

Dans ces conditions, on observe à la dose de 250 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples 31, 34, 41, 67.

- 35 **Exemple L** : Test *in vivo* sur *Venturia inaequalis* (tavelure du pommier) :

Une suspension aqueuse, de concentration 2 g/l, de la matière active testée est

obtenue par broyage fin de celle-ci dans le mélange suivant :

- eau

- mélange spécifique à base de Soprophor BS4, de cyclohexanone, de N-méthyl pyrrolidone et de N-octyl pyrrolidone à raison de 100 µl pour 10 mg de matière active.

- 5 Cette suspension aqueuse est ensuite diluée par de l'eau de manière à obtenir la concentration désirée en matière active.

Des pommiers (variété Golden) en godets sont traités au stade 5 -6 feuilles (4 à 6 semaines après le semis) par pulvérisation de la suspension aqueuse décrite ci-dessus.

- Des plants, utilisés comme témoins sont traités par une solution aqueuse ne contenant
10 pas la matière active.

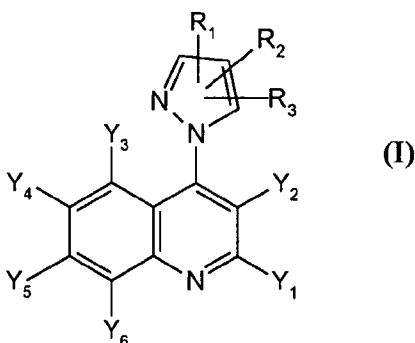
Après 24 heures, les plants sont contaminés par une solution aqueuse de *Venturia inaequalis* (suspension à 150 000 spores/ml).

La notation est effectuée 15 à 20 jours après la contamination, en comparaison avec les plants témoins.

- 15 Dans ces conditions, on observe à la dose de 250 g/ha, une protection bonne (au moins 50%) ou totale avec les composés décrits dans les exemples 31, 34 et 67.

REVENDICATIONS

5 1. Composés de formule générale (I) :



dans laquelle :

- R₁ et R₂ sont différents et sont choisis parmi un radical alkyle, alkoxy,
 10 alkylthio, alkylsulfinyle, alkylsulfonyle, alkoxysulfonyle, alkényle,
 alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cycloalkyle,
 hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle,
 alkénylcarbonyle, alkynylcarbonyle, alkylcarbonyloxy, alkénylcarbonyloxy,
 alkynylcarbonyloxy, alkoxycarbonyle, alkoxyalkylcarbonyle,
 15 alkényloxycarbonyle, alkynyloxycarbonyle, cycloalkyl-carbonyle,
 hétérocyclylcarbonyl, cycloalkyl-oxycarbonyle, cycloalkylalkyloxy-
 carbonyle, hétérocyclyl-oxycarbonyle, hétérocyclylalkoxycarbonyle,
 thioalkylthiocarbonyle, alkoxythiocarbonyle, thioalkyle,
 un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle,
 20 le radical hydroxy, le radical mercapto, le radical carboxy, le radical nitro, le
 radical cyano, le radical thiocyanato, le radical azido, un radical NR₄R₅,
 C(=O)NR₄R₅, C(=S)NR₄R₅, un radical C(=NR₄)R₅, un atome d'halogène, le
 radical sulfonyle, le radical sulfinyle, le radical sulfanyle, le radical
 phosphoryle et le radical phosphone,

25

ou bien

R₁ et R₂ peuvent former ensemble un cycle de 4 à 7 atomes, contenant 2 à 3
 atomes d'oxygène et/ou d'azote, éventuellement substitué par un ou
 plusieurs radicaux choisis parmi halogène, alkyle, haloalkyle, alkoxy, amino
 30 et NR₄R₅ ;

- 5
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R_3 est choisi parmi l'hydrogène, un radical alkyle, alkoxy, alkylthio, alkylsulfinyle, alkylsulfonyle, alkoxysulfonyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cycloalkyle, hétérocyclyle, cycloalkylcarbonyle, hétérocyclylcarbonyl, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkénylcarbonyle, alkynylcarbonyle, alkylcarbonyloxy, alkénylcarbonyloxy, alkynylcarbonyloxy, alkoxycarbonyle, alkényloxycarbonyle, alkynyloxycarbonyle, cycloalkyl-oxycarbonyle, cycloalkylalkyloxycarbonyle, hétérocyclyl-oxycarbonyle, hétérocyclylalkoxy-carbonyle, un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle, le radical hydroxy, le radical mercapto, le radical carboxy, le radical nitro, le radical cyano, le radical thiocyanato, le radical azido, un radical NR_4R_5 , $C(=O)NR_4R_5$, $C(=S)NR_4R_5$ et un radical $C(=NR_4)R_5$,
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R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical alkyle, alkoxy, alkylthio, alkylsulfinyle, alkylsulfonyle, alkoxysulfonyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cyanoalkyle, alkoxyalkyle, alkoxycarbonylalkyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkénylcarbonyle, alkynylcarbonyle, alkoxycarbonyle, alkényloxycarbonyle, alkynyloxycarbonyle, cycloalkyloxycarbonyle, cycloalkylalkyl-oxycarbonyle, hétérocyclyloxycarbonyle, hétérocyclylalkoxycarbonyle, un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle, arylalkyle, hétéroarylalkyle, le radical mercapto, le radical carboxy, le radical nitro, le radical cyano, le radical thiocyanato, le radical azido, un radical OR_6 , amino, alkylamino, dialkylamino, aminoalkyle, alkylaminoalkyle et dialkylaminoalkyle, hydrazino,

ou bien

R_4 et R_5 peuvent former ensemble un cycle de 4 à 7 atomes, contenant 2 à 3 atomes d'oxygène et/ou d'azote, éventuellement substitué par un ou plusieurs radicaux choisis parmi halogène, alkyle, haloalkyle, alkoxy, amino et NR_7R_8 ;
- R_6 représente l'hydrogène, un radical alkyle, aryle, hétéroaryle, arylalkyle,

hétéroarylalkyle, cycloalkyle, cycloalkylalkyle, hétérocyclyle,
hétérocyclyalkyle et alkoxycarbonylalkyle,

- 5 • R₇ et R₈, identiques ou différents, sont choisis parmi l'hydrogène, un radical alkyle, alkoxy, alkylthio, alkylsulfinyle, alkylsulfonyle, alkoxysulfonyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, cyanoalkyle, alkoxyalkyle, alkoxycarbonylalkyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclyalkyle, alkylcarbonyle, alkénylcarbonyle, alkynylcarbonyle, alkoxycarbonyle, alkényloxycarbonyle, 10 alkynyloxycarbonyle, cycloalkyloxycarbonyle, cycloalkylalkyloxycarbonyle, hétérocyclyloxycarbonyle, hétérocyclylalkoxycarbonyle, un radical aryle, hétéroaryle, arylcarbonyle, hétéroarylcarbonyle, arylalkyle, hétéroarylalkyle, 15 le radical mercapto, le radical carboxy, le radical nitro, le radical cyano, le radical thiocyanato, le radical azido, un radical OR₆, amino, alkylamino, dialkylamino, aminoalkyle, alkylaminoalkyle et dialkylaminoalkyle, hydrazino, 20 ou bien, R₇ et R₈ peuvent former ensemble un cycle de 4 à 7 atomes, contenant 2 à 3 atomes d'oxygène et/ou d'azote, éventuellement substitué par un ou plusieurs radicaux choisis parmi halogène, alkyle, haloalkyle, alkoxy et amino ;
- 25 • les radicaux Y₁, Y₂, Y₃, Y₄, Y₅ et Y₆ sont choisis indépendamment les uns des autres parmi l'atome d'hydrogène, un atome d'halogène; le radical hydroxy, mercapto, nitro, thiocyanato, azido, cyano ou pentafluorosulfonyle, un radical alkyle, haloalkyle, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyle, haloalkoxyalkyle, alkylthioalkyle, haloalkylthioalkyle, 30 cyanoalkyle, cyanoalkoxy, cyanoalkylthio, alkylsulfinyle, haloalkylsulfinyle, alkylsulfonyle, haloalkylsulfonyle, alkoxysulfonyle, un groupe cycloalkyle, halocycloalkyle, alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio, alkynylthio, 35 un radical aryle ou hétéroaryle éventuellement substitué, un radical amino, N-alkylamino, N,N-dialkylamino, acylamino, amino-alkyle, N-alkylaminoalkyle, N,N-dialkylaminoalkyle, acylaminoalkyle,

le radical carboxy, le radical carbamoyle, un radical N-alkylcarbamoyle, N,N-dialkylcarbamoyle, alkoxycarbonyle et un radical alkylcarbonyle,

ou bien

5 deux radicaux adjacents choisis parmi Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 pouvant également former, ensemble et avec les deux atomes de carbone qui les portent, un cycle aromatique à 6 chaînons, ou

deux radicaux adjacents choisis parmi Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 pouvant également former ensemble un radical divalent méthylène-di-oxy ;

10

- l'ensemble des radicaux définis ci-dessus et possédant une chaîne hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle, alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, mercapto, NR_4R_5 , cyano, nitro, alkyle, alkoxyalkyle, aryle, hétéroaryle, halogène, alkoxy, alkylthio, alkylcarbonyle, alkylcarbonyloxy, alkénylcarbonyle, alkénylcarbonyloxy, alkynylcarbonyle, alkynylcarbonyloxy, arylcarbonyl, arylcarbonyloxy, hétéroarylcarbonyl, hétéroarylcarbonyloxy, aryloxy, arylthio, hétéroaryloxy, hétéroarylthio, halogénoalkoxy, perhalogénoalkoxy, cyanoalkylcarbonyloxy, cycloalkyle, hétérocyclyle, cycloalkylcarbonyle, cycloalkylcarbonyloxy, hétérocyclylcarbonyle, hétérocyclylcarbonyloxy, aryloxyalkylcarbonyloxy, alkylcarbonylalkylcarbonyloxy, alkoxycarbonyl-alkylcarbonyloxy, arylcarbonylcarbonyloxy, hétéroarylcarbonyl-carbonyloxy, alkoxyalkoxyalkylcarbonyloxy et alkylthioalkylcarbonyloxy,
 - l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, mercapto, oxo, cyano, nitro, cyanato, thiocyanato, formyle, propylène-diyle, amino, alkylamino, dialkylamino, pentafluorosulfonyl, aryle, hétéroaryle, halogène, alkyle, haloalkyle, perhaloalkyle, alkényle, alkynyle, alkoxy, alkylthio, haloalkoxy, perhaloalkoxy, alkoxyalkyle, alkylcarbonyle, alkoxycarbonyle, alkylcarbonyloxy, alkénylcarbonyle, alkénylcarbonyloxy, alkynylcarbonyle, alkynylcarbonyloxy, arylcarbonyl, arylcarbonyloxy, hétéroarylcarbonyle, hétéroarylcarbonyloxy, aryloxy, arylthio, hétéroaryloxy, hétéroarylthio, cycloalkyle, hétérocyclyle, cycloalkylcarbonyle et hétérocyclylcarbonyle,
- 15
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leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles formes tautomères,

ainsi que les sels, les N-oxydes et les complexes métalliques et métalloïdiques des composés de formule (I) tels qu'ils viennent d'être définis,

5 à l'exception des composés suivants :

- le trans-(+/-)-6-[2-[1-(9-acridinyl)-5-(4-fluorophenyl)-3-(1-methylethyl)-1*H*-pyrazol-4-yl]ethyl]tetrahydro-4-hydroxy-2*H*-pyran-2-one ;
- le trans-(+/-)-6-[2-[1-(9-acridinyl)-5-(4-fluorophenyl)-3-(1-methylethyl)-1*H*-pyrazol-4-yl]ethenyl]tetrahydro-4-hydroxy-2*H*-pyran-2-one ;
- 10 • le 3-méthyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-trifluorométhyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-phenyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-(2-thienyl)-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- les 1-(méthyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;
- 15 • les 1-(trifluorométhyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;
- les 1-(phenyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;
- les 1-[(2-thienyl)-quinolin-4-yl]-3-méthyl-5-trifluorométhylpyrazoles ;
- l'endo-1-(7-chloro-4-quinoliny)-5-méthyl-N-(9-azabicyclo[3,3,1]non-3-yl)-1*H*-pyrazole-3-carboxamide ;
- 20 • le 5-amino-1-(7-chloro-4-quinoliny)-1*H*-pyrazole-4-carbonitrile ;
- le 4-acetyl-1-(7-chloro-4-quinoliny)-5-méthyl-1*H*-pyrazole ;
- l'acide 5-méthyl-1-(4-quinoliny)-1*H*-pyrazole-4-carboxylique ;
- l'acide 5-cyclopropyl-1-(4-quinoliny)-1*H*-pyrazole-4-carboxylique.

25 2. Composés selon la revendication 1 présentant l'une et/ou l'autre des caractéristiques suivantes prises isolément ou en combinaison :

- R₁ et R₂ sont différents et sont choisis parmi un radical alkyle, alkoxyalkyle, alkylthioalkyle, hydroxyalkyle, aminoalkoxyalkyle, N-alkylaminoalkoxyalkyle, N,N-dialkylaminoalkoxyalkyle, aminoalkyl-30 thioalkyle, N-alkylaminoalkyl-thioalkyle, N,N-dialkylaminoalkylthioalkyle, alkényle, cycloalkyle, cycloalkylcarbonyle, hétérocyclylcarbonyl, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkylcarbonyloxy, alkylcarbonyloxyalkyle, alkénylcarbonyloxyalkyle, alkynylcarbonyloxyalkyle, alkoxycarbonyle, cycloalkylalkoxycarbonyle,

35

un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, aryloxyalkyle, hétéroaryloxyalkyle, arylcarbonyle, hétéroarylcarbonyle, arylcarbonyl-

oxyalkyle, hétéroarylcabonyloxyalkyle,
le radical hydroxy, le radical carboxy, le radical nitro, le radical cyano, un
radical NR_4R_5 , $\text{CH}_2\text{NR}_4\text{R}_5$, $\text{C}(=\text{O})\text{NR}_4\text{R}_5$, et un radical $\text{C}(=\text{NR}_4)\text{R}_5$,

- 5 • R_3 est choisi parmi l'hydrogène, un radical alkyle, alkoxy, alkoxyalkyle, alkylthio, alkényle, alkynyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclalkyle, alkylcarbonyl, alkylcarbonyloxy, alkoxycarbonyl, le radical hydroxy, le radical mercapto, le radical carboxy, et un radical NR_4R_5 ,
- 10 • R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical alkyle, alkoxy, alkoxyalkyle, alkylthio, alkényle, alkynyle, alkényloxy, alkynyloxy, cyanoalkyle, alkoxyalkyle, alkoxycarbonylalkyle, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclalkyle, alkylcarbonyl, alkoxycarbonyl,
- 15 un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, le radical mercapto, le radical cyano, un radical OR_6 , amino, alkylamino, dialkylamino, aminoalkyle, alkylaminoalkyle et dialkylaminoalkyle,
- 20 • R_6 représente l'hydrogène, un radical alkyle, aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, cycloalkyle, cycloalkylalkyle, hétérocyclyle, hétérocyclalkyle, et alkoxycarbonylalkyle,
- 25 • les radicaux Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont choisis indépendamment les uns des autres parmi l'atome d'hydrogène, un atome d'halogène, le radical hydroxy, mercapto, nitro, cyano ou pentafluorosulfonyl, un radical alkyle, haloalkyle, alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkoxyalkyle, haloalkoxyalkyle, cyanoalkyle, cyanoalkoxy, cyanoalkylthio, un radical alkényle, alkynyle, alkényloxy, alkynyloxy, alkénylthio,
- 30 alkynylthio, un radical amino, N-alkylamino, N,N-dialkylamino, aminoalkyle, N-alkylaminoalkyle, N,N-dialkylaminoalkyle, le radical carboxy, alkoxycarbonyl et un radical alkylcarbonyl,
- 35 ou bien
deux radicaux adjacents choisis parmi Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 pouvant également former, ensemble et avec les deux atomes de carbone qui les

portent, un cycle aromatique à 6 chaînons,

- 5 • l'ensemble des radicaux définis ci-dessus et possédant une chaîne hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle, alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy, mercapto, amino, N-alkylamino, N,N-dialkylamino, cyano, nitro, aryle, hétéroaryle, halogène, alkoxy, alkylthio, aryloxy, arylthio, hétéroaryloxy, hétéroarylthio, halogénoalkoxy, perhalogénoalkoxy, cyanoalkyl-

10 carbonyloxy, cycloalkyle, hétérocyclyle, cycloalkylcarbonyle, cycloalkylcarbonyloxy, hétérocyclylcarbonyle, hétérocyclylcarbonyloxy, aryloxyalkylcarbonyloxy, alkylcarbonylalkylcarbonyloxy, alkoxycarbonylalkylcarbonyloxy, arylcarbonylcarbonyloxy, hétéroarylcarbonylcarbonyloxy, alkoxyalkoxyalkylcarbonyloxy et

15 alkylthioalkylcarbonyloxy,
- l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi oxo, cyano, nitro, formyle,

20 propylène-diyle, amino, N-alkylamino, N,N-dialkylamino, aryle, hétéroaryle, halogène, alkyle, haloalkyle, perhaloalkyle, alkoxy, alkylthio, haloalkoxy, perhaloalkoxy, alkoxyalkyle, alkylcarbonyle, alkoxycarbonyle, aryloxy, cycloalkyle et hétérocyclyle,
- 25 leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles formes tautomères,

 ainsi que les sels, les N-oxydes et les complexes métalliques et métalloïdiques de ces composés.
- 30 3. Composés selon l'une des revendications précédentes, présentant l'une et/ou l'autre des caractéristiques suivantes prises isolément ou en combinaison :

 - R₁ et R₂ sont différents et sont choisis parmi un radical alkyle, alkoxyalkyle, alkylthioalkylke, hydroxyalkyle, aminoalkoxyalkyle, N-alkylaminoalkoxyalkyle, N,N-dialkylaminoalkoxyalkyle, aminoalkyl-

35 thioalkyle, N-alkylaminoalkyl-thioalkyle, N,N-dialkylaminoalkylthioalkyle, alkényle, cycloalkylcarbonyle, hétérocyclylcarbonyl, cycloalkylalkyle, hétérocyclylalkyle, alkylcarbonyle, alkylcarbonyloxy,

alkylcarbonyloxyalkyle, alkoxycarbonyle, cycloalkylalkoxycarbonyle,
 un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, aryloxyalkyle,
 hétéroaryloxyalkyle, arylcarbonyle, hétéroarylcarbonyle,
 le radical carboxy, un radical NR_4R_5 , $\text{CH}_2\text{NR}_4\text{R}_5$, $\text{C}(=\text{O})\text{NR}_4\text{R}_5$, et un radical
 5 $\text{C}(=\text{NR}_4)\text{R}_5$,

- R_3 est choisi parmi l'hydrogène, un radical alkyle, alkoxy, alkoxyalkyle,
 alkylthio, cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle,
 alkoxycarbonyle,
 10 le radical carboxy, et un radical NR_4R_5 ,
- R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical
 alkyle, alkoxy, alkoxyalkyle, alkoxyalkyle, alkoxycarbonylalkyle,
 cycloalkyle, hétérocyclyle, cycloalkylalkyle, hétérocyclylalkyle,
 15 un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle,
 et un radical OR_6 ,
- R_6 représente l'hydrogène, un radical aryle, hétéroaryle, arylalkyle,
 hétéroarylalkyle, cycloalkyle, cycloalkylalkyle, hétérocyclyle, et
 20 hétérocyclyalkyle,
- les radicaux Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont choisis indépendamment les uns
 des autres parmi l'atome d'hydrogène, un atome d'halogène, le radical
 hydroxy, un radical alkyle, haloalkyle, alkoxy, haloalkoxy, alkoxyalkyle et
 25 haloalkoxyalkyle,
- l'ensemble des radicaux définis ci-dessus et possédant une chaîne
 hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle,
 alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs
 30 groupes ou radicaux, identiques ou différents, choisis parmi hydroxy,
 halogène, alkoxy et halogénoalkoxy,
- l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent
 éventuellement être substitués par un ou plusieurs groupes ou radicaux,
 35 identiques ou différents, choisis parmi oxo, halogène, alkyle, haloalkyle,
 perhaloalkyle, alkoxy, haloalkoxy, perhaloalkoxy, alkoxyalkyle,
 alkylcarbonyle, alkoxycarbonyle et aryloxy,

leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles formes tautomères,

ainsi que les sels, les N-oxydes et les complexes métalliques et
5 métalloïdiques de ces composés.

4. Composés selon l'une des revendications précédentes, présentant l'une et/ou l'autre des caractéristiques suivantes prises isolément ou en combinaison :

- R_1 et R_2 sont différents et sont choisis parmi un radical alkyle,
10 alkoxyalkyle, hydroxyalkyle, cycloalkylcarbonyle, hétérocyclcarbonyl, alkylcarbonyle, alkylcarbonyloxy, alkylcarbonyloxyalkyle, alkoxycarbonyle, cycloalkylalkoxycarbonyle, un radical aryle, hétéroaryle, arylalkyle, hétéroarylalkyle, aryloxyalkyle, hétéroaryloxyalkyle,
15 le radical carboxy et un radical $C(=O)NR_4R_5$,
- R_3 représente l'hydrogène,
- R_4 et R_5 , identiques ou différents, sont choisis parmi l'hydrogène, un radical
20 alkyle, alkoxy et alkoxycarbonylalkyle,
- les radicaux Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont choisis indépendamment les uns des autres parmi l'atome d'hydrogène, un atome d'halogène, un radical alkyle, haloalkyle et alkoxy,
25
- l'ensemble des radicaux définis ci-dessus et possédant une chaîne hydrocarbonée (alkyle, alkoxy, cycloalkyle, hétérocycloalkyle, alkényle, alkynyle, etc.) peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi hydroxy,
30 halogène, alkoxy et haloalkoxy,
- l'ensemble des radicaux aryle et hétéroaryle définis ci-dessus peuvent éventuellement être substitués par un ou plusieurs groupes ou radicaux, identiques ou différents, choisis parmi oxo, halogène, alkyle, haloalkyle,
35 alkoxy, haloalkoxy, perhaloalkoxy et alkoxycarbonyle,

leurs éventuels isomères géométriques et/ou optiques, leurs éventuelles

formes tautomères,

ainsi que les sels, les N-oxydes et les complexes métalliques et métalloïdiques de ces composés.

- 5 5. Composés selon l'une des revendications précédentes, choisis parmi le ou la :
- 1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
 - 3-(méthoxyméthyl)-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazole-4-
10 carboxylate de méthyle ;
 - 1-(7-chloro-4-quinolyl)-5-(3-nitrophényl)-1*H*-pyrazole-4-carboxylate méthyle ;
 - 1-(7-chloro-4-quinolyl)-*N,N*-diéthyl-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxamide ;
 - 15 • 1-(7-chloro-4-quinolyl)-*N*-méthoxy-5-(méthoxyméthyl)-*N*-méthyl-1*H*-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolyl)-5-(2-méthoxyéthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
 - 5-(2-méthoxyéthyl)-1-(7-méthoxy-4-quinolyl)-1*H*-pyrazole-4-carboxylate
20 de méthyle ;
 - 1-[2,8-bis(trifluorométhyl)-4-quinolyl]-*N*-méthoxy-3-(méthoxyméthyl)-*N*-méthyl-1*H*-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolyl)-3-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
 - 25 • 1-(6-fluoro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de méthyle ;
 - 1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxylate de 2-éthoxyéthyle ;
 - *N*-méthoxy-3-(méthoxyméthyl)-*N*-méthyl-1-[8(trifluorométhyl)-4-
30 quinolyl]-1*H*-pyrazole-4-carboxamide ;
 - [1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-yl](1,3-thiazolidin-3-yl)méthanone ;
 - 2-[1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazol-4-yl]-2-propanol ;
 - 35 • 1-(7-chloro-4-quinolyl)-*N*-méthoxy-5-(méthoxyméthyl)-*N*-propyl-1*H*-pyrazole-4-carboxamide ;
 - 5-({4-méthoxycarbonyl)-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazol-5-

- yl)méthoxy)isophtalate de diméthyle ;
- 1-(7-chloro-4-quinolyl)-*N*-isopropyl-*N*-méthoxy-5-(méthoxyméthyl)-1*H*-pyrazole-4-carboxamide ;
 - 4-[[1-(7-chloro-4-quinolyl)-5-(méthoxyméthyl)-1*H*-pyrazole-4-yl]carbonyl](méthoxy)amino]butanoate de méthyle ;
 - 5-[(heptanoyloxy)méthyl]-1-[8-(trifluorométhyl)-4-quinolyl]-1*H*-pyrazole-4-carboxylate de méthyle ;
 - la 7-chloro-4-{5-méthoxyméthyl}-4-[5-trifluorométhyl]-1,2,4-oxadiazol-3-yl]-1*H*-pyrazol-1-yl} quinoléine ;
 - methyl 1-(7-chloro-4-quinoliny)-5-[(1 ;1-dimethylethyl)sulfanyl]methyl]-1*H*-pyrazole-4-carboxylate ;
 - 1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1*H*-pyrazole-4-carbaldehyde ;
 - [1-(7-chloro-4-quinoliny)-4-(1-phenylethenyl)-1*H*-pyrazol-5-yl]methyl methyl ether ;
 - 1-{3-[(methyloxy)methyl]-1-[8-(trifluorométhyl)-4-quinoliny]-1*H*-pyrazol-4-yl}ethanone ;
 - methyl 3-[(methyloxy)methyl]-5-(methylsulfanyl)-1-[8-(trifluorométhyl)-4-quinoliny]-1*H*-pyrazole-4-carboxylate ;
 - methyl 5-chloro-3-[(methyloxy)methyl]-1-[8-(trifluorométhyl)-4-quinoliny]-1*H*-pyrazole-4-carboxylate ;
 - (1*E*)-1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1*H*-pyrazol-4-yl}ethanone oxime ;
 - 1-(2 ;7-diméthyl-4-quinoliny)-*N*-methyl-*N*-(methyloxy)-5-[(methyloxy)methyl]-1*H*-pyrazole-4-carboxamide ;
 - *N*-methyl-1-[2-méthyl-8-(1-méthylethyl)-4-quinoliny]-*N*-(methyloxy)-5-[(methyloxy)methyl]-1*H*-pyrazole-4-carboxamide ;
 - *N*-methyl-*N*-(methyloxy)-5-[(methyloxy)methyl]-1-[2-méthyl-7-(trifluorométhyl)-4-quinoliny]-1*H*-pyrazole-4-carboxamide ;
 - *N*-methyl-*N*-(methyloxy)-5-[(methyloxy)methyl]-1-(2 ;5 ;7-triméthyl-4-quinoliny)-1*H*-pyrazole-4-carboxamide ;
 - 1-(7-chloro-2 ;8-diméthyl-4-quinoliny)-*N*-methyl-*N*-(methyloxy)-5-[(methyloxy)methyl]-1*H*-pyrazole-4-carboxamide ;
 - 1-(6 ;8-dichloro-2-méthyl-4-quinoliny)-*N*-methyl-*N*-(methyloxy)-5-[(methyloxy)methyl]-1*H*-pyrazole-4-carboxamide ;
 - *N*-methyl-*N*-(methyloxy)-5-[(methyloxy)methyl]-1-(8-méthyl-4-quinoliny)-1*H*-pyrazole-4-carboxamide ;

- 1-(2 ;8-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-[2-methyl-8-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- 5 • 1-(6-chloro-2 ;8-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-(2-methyl-4-quinoliny)-1H-pyrazole-4-carboxamide ;
- 10 • N-methyl-1-[2-methyl-8-(methyloxy)-4-quinoliny]-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1-(2 ;6 ;8-trimethyl-4-quinoliny)-1H-pyrazole-4-carboxamide ;
- 1-[5-chloro-2-methyl-8-(methyloxy)-4-quinoliny]-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 15 • 1-(5 ;7-dichloro-4-quinoliny)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 5-(hydroxymethyl)-N-methyl-N-(methyloxy)-1-[8-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- 1-(6-chloro-2 ;8-dimethyl-4-quinoliny)-N-methyl-N-(methyloxy)-5-[2-(methyloxy)ethyl]-1H-pyrazole-4-carboxamide ;
- 20 • N-methyl-N-(methyloxy)-5-[2-(methyloxy)ethyl]-1-[8-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-5-[2-(methyloxy)ethyl]-1-[7-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- 25 • N ;5-dimethyl-N-(methyloxy)-1-[2-methyl-8-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbaldehyde O-methyloxime ;
- 5-(bromomethyl)-1-(5 ;7-dichloro-4-quinoliny)-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 30 • 1-(7-chloro-4-quinoliny)-3-(dibromomethyl)-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanol ;
- 35 • (1E)-1-{3-[(methyloxy)methyl]-1-[8-(trifluoromethyl)-4-quinoliny]-1H-pyrazol-4-yl}ethanone O-(cyclopropylmethyl)oxime ;
- N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-[7-(trifluoromethyl)-4-

- quinoliny]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-[2-(trifluoromethyl)-4-quinoliny]-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinoliny)-N-methyl-N-(methyloxy)-3-
5 [(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - methyl 3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-4 ;5-dihydro-5-isoxazolecarboxylate ;
 - 1-(7-chloro-4-quinoliny)-N-(cyclopropylcarbonyl)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 10 • ethyl 3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-oxopropanoate ;
 - 1-(7-chloro-4-quinoliny)-N-methyl-N-(methyldisulfanyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinoliny)-N-(ethyldisulfanyl)-N-methyl-5-
15 [(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinoliny)-N-methyl-N-[(1-methylethyl)disulfanyl]-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - ethyl 1-(7-chloro-4-quinoliny)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbimidothioate ;
 - 20 • (1E)-1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-1-propanone O-methyloxime ;
 - (3E)-4-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-buten-2-one ;
 - ethyl (2Z ;4E)-5-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-hydroxy-2 ;4-pentadienoate ;
 - 25 • 2-propenyl (2E)-3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-2-propenoate ;
 - 1-(7-chloro-4-quinoliny)-N-(ethyloxy)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 30 • 4-(3-[(methyloxy)methyl]-4-{5-[(methyloxy)methyl]-3-isoxazolyl})-1H-pyrazol-1-yl)-8-(trifluoromethyl)quinoline ;
 - 7-chloro-4-{4-[(ethyloxy)methyl]-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}quinoline ;
 - (Z)-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-
35 yl}[(methyloxy)imino]methyl methanesulfonate ;
 - 1-(7-chloro-4-quinoliny)-N-methyl-5-[(methyloxy)methyl]-N-(methyldisulfanyl)-1H-pyrazole-4-carboxamide ;

- 1-(7-chloro-4-quinolinyl)-N-(ethylsulfanyl)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- {1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}acetonitrile ;
- 5 • 3-(hydroxymethyl)-N ;N-dimethyl-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
- {1-(7-chloro-4-quinolinyl)-4-[3-(4-fluorophenyl)-1 ;2 ;4-oxadiazol-5-yl]-1H-pyrazol-5-yl}methyl methyl ether ;
- 10 • 1-(7-chloro-4-quinolinyl)-N-(methyloxy)-N ;5-bis[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- [1-(7-chloro-4-quinolinyl)-4-(3-phenyl-1 ;2 ;4-oxadiazol-5-yl)-1H-pyrazol-5-yl]methyl methyl ether ;
- 2-oxiranylmethyl 1-(7-chloro-4-quinolinyl)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboximidoate ;
- 15 • 1-(7-chloro-4-quinolinyl)-N'-[(cyclopropylmethyl)oxy]-5-[(methyloxy)methyl]-1H-pyrazole-4-carboximidamide ;
- 1-(7-chloro-4-quinolinyl)-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboximidoyl chloride ;
- 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-N ;N-dimethyl-4 ;5-dihydro-5-isoxazolecarboxamide ;
- 20 • (1Z)-1-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanone O-(2-methylpropanoyl)oxime ;
- (1E)-1-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanone O-(cyclopropylcarbonyl)oxime ;
- 25 • 1-(8-fluoro-4-quinolinyl)-N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-(7-methyl-4-quinolinyl)-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-methyl-N-(methyloxy)-5-({[2-(methyloxy)-5-nitrophenyl]oxy}methyl)-1H-pyrazole-4-carboxamide ;
- 30 • 5-{[(2-bromo-3-pyridinyl)oxy]methyl}-N-methyl-N-(methyloxy)-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
- 5-{[(4'-bromo[1 ;1'-biphenyl]-4-yl)oxy]methyl}-N-methyl-N-(methyloxy)-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
- 35 • 5-chloro-N-methyl-N-(methyloxy)-3-[(methyloxy)methyl]-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxamide ;
- methyl {[1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-

- yl}carbonyl)(methylamino]oxy}(oxo)acetate ;
- 1-{1-(7-fluoro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-1-propanone ;
 - (1E)-1-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}ethanone O-[2-(methyloxy)acetyl]oxime ;
 - 4-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}benzaldehyde ;
 - 1-(7-chloro-4-quinolinyl)-5-([2-(ethylsulfanyl)phenyl]oxy)methyl-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-N-(propyloxy)-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-N-(2-propenyloxy)-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-N-[(1-methylpropyl)oxy]-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolinyl)-N-methyl-N-[(1-methylethyl)oxy]-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - methyl 4-[[[1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl]carbonyl)(methylamino]oxy]butanoate ;
 - N-(3-butenyloxy)-1-(7-chloro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
 - 1-(7-chloro-4-quinolinyl)-5-[(ethyloxy)methyl]-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
 - 4-{4-{4 ;5-bis[(methyloxy)methyl]-3-isoxazolyl}-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}-7-bromoquinoline ;
 - (3-{1-(6-fluoro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl acetate ;
 - 4-{4-{4 ;5-bis[(methyloxy)methyl]-3-isoxazolyl}-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}-6-fluoroquinoline ;
 - 7-ethyl-4-(5-[(methyloxy)methyl]-4-{5-[(tetrahydro-2H-pyran-2-yloxy)methyl]-3-isoxazolyl}-1H-pyrazol-1-yl)quinoline ;
 - 4-{4-{4 ;5-bis[(methyloxy)methyl]-3-isoxazolyl}-5-[(methyloxy)methyl]-1H-pyrazol-1-yl}-7-ethylquinoline ;
 - 3-[[[3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl]oxy]propanenitrile ;
 - methyl 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-4-methyl-5-isoxazolecarboxylate ;

- 1 ;1-dimethylethyl 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolecarboxylate ;
- 3-{[(3-{1-(7-ethyl-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl]oxy}propanenitrile ;
- 5 • {1-(7-chloro-4-quinolinyl)-4-[2-(trifluoromethyl)phenyl]-1H-pyrazol-5-yl}methyl methyl ether ;
- 7-chloro-4-(5-[(methyloxy)methyl]-4-{4-[(trifluoromethyl)oxy]phenyl}-1H-pyrazol-1-yl)quinoline ;
- methyl 5-[(methyloxy)methyl]-1-(6 ;7 ;8-trichloro-4-quinolinyl)-1H-pyrazole-4-carboxylate ;
- 10 • 1-(7-chloro-4-quinolinyl)-N-methyl-5-{[(1-methylethyl)oxy]methyl}-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- methyl 3-[(methyloxy)methyl]-5-(2-thienyl)-1-[8-(trifluoromethyl)-4-quinolinyl]-1H-pyrazole-4-carboxylate ;
- 15 • 7-chloro-4-(5-[(methyloxy)methyl]-4-{3-[(methyloxy)methyl]-1 ;2 ;4-oxadiazol-5-yl}-1H-pyrazol-1-yl)quinoline ;
- [1-(7-chloro-4-quinolinyl)-4-(1 ;3-thiazol-2-yl)-1H-pyrazol-5-yl]methyl methyl ether ;
- [1-(7-chloro-4-quinolinyl)-4-(4 ;5-dihydro-1 ;3-thiazol-2-yl)-1H-pyrazol-5-yl]methyl methyl ether ;
- 20 • 1 ;1-dimethylethyl 1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxylate ;
- 1-(7-cyano-4-quinolinyl)-N-methyl-N-(methyloxy)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 25 • [4-[5-(bromomethyl)-3-isoxazolyl]-1-(7-bromo-4-quinolinyl)-1H-pyrazol-5-yl]methyl methyl ether ;
- 1-(7-chloro-4-quinolinyl)-N'-methyl-5-[(methyloxy)methyl]-N'-phenyl-1H-pyrazole-4-carbohydrazide ;
- 1-(7-chloro-4-quinolinyl)-N'-(2 ;5-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
- 30 • 1-(7-chloro-4-quinolinyl)-N'-(1 ;1-dimethylethyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
- (1-(7-chloro-4-quinolinyl)-4-{[methyl(methyloxy)amino]carbonyl}-1H-pyrazol-5-yl)methyl 2-methylpropanoate ;
- 35 • N-ethyl-1-(6-fluoro-4-quinolinyl)-N-methyl-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-(cyclopropylmethyl)-N-methyl-5-

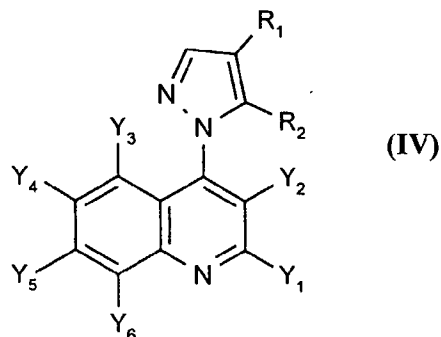
- [(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-4 ;6-dimethyl-4H-1 ;2 ;4-oxadiazin-5(6H)-one ;
- N-(4-chloro-2-butynyl)-1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carboxamide ;
- methyl 1-(7-chloro-4-quinolinyl)-5-(methyloxy)-1H-pyrazole-4-carboxylate ;
- 1-(7-chloro-4-quinolinyl)-5-(ethylsulfanyl)-N-methyl-N-(methyloxy)-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-N-(4-morpholinyl)-1H-pyrazole-4-carboxamide ;
- 1-(7-chloro-4-quinolinyl)-N-methyl-N-(methyloxy)-5-(methylsulfanyl)-1H-pyrazole-4-carboxamide ;
- (1-(7-chloro-4-quinolinyl)-4-{[methyl(methyloxy)amino]carbonyl}-1H-pyrazol-5-yl)methyl cyclopropanecarboxylate ;
- (1-(7-chloro-4-quinolinyl)-4-{[methyl(methyloxy)amino]carbonyl}-1H-pyrazol-5-yl)methyl 2-thienylacetate ;
- 7-chloro-4-(5-[(methyloxy)methyl]-4-{1-[3-(methyloxy)propyl]-1H-imidazol-5-yl}-1H-pyrazol-1-yl)quinoline ;
- [1-(7-chloro-4-quinolinyl)-4-(1-methyl-1H-imidazol-5-yl)-1H-pyrazol-5-yl]methyl methyl ether ;
- {1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}[(trimethylsilyl)oxy]acetonitrile ;
- [1-(7-bromo-4-quinolinyl)-4-(1-piperidinylcarbonyl)-1H-pyrazol-5-yl]methyl methyl ether ;
- methyl {4-(1-piperidinylcarbonyl)-1-[7-(trifluoromethyl)-4-quinolinyl]-1H-pyrazol-5-yl}methyl ether ;
- 5-amino-1-(7-chloro-4-quinolinyl)-1H-pyrazole-4-carbonitrile ;
- 3-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-2-thiophenecarbaldehyde ;
- [1-(7-chloro-4-quinolinyl)-4-(5-ethenyl-1 ;3-oxazol-2-yl)-1H-pyrazol-5-yl]methyl methyl ether ;
- 1-(2-{1-(7-chloro-4-quinolinyl)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-1 ;3-oxazol-5-yl)ethyl acetate ;
- [1-(7-bromo-4-quinolinyl)-4-(2-isoxazolidinylcarbonyl)-1H-pyrazol-5-yl]methyl methyl ether ;
- {4-(2-isoxazolidinylcarbonyl)-1-[7-(trifluoromethyl)-4-quinolinyl]-1H-

- pyrazol-5-yl}methyl methyl ether ;
- [1-(7-ethyl-4-quinoliny)-4-(2-isoxazolidinylcarbonyl)-1H-pyrazol-5-yl]methyl methyl ether ;
 - [1-(6-fluoro-4-quinoliny)-4-(2-isoxazolidinylcarbonyl)-1H-pyrazol-5-yl]methyl methyl ether ;
 - N'-(2-chlorophenyl)-1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinoliny)-N'-(2 ;4-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinoliny)-N'-(2 ;6-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-N'-(3-methylphenyl)-1H-pyrazole-4-carbohydrazide ;
 - N'-(3-chlorophenyl)-1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - N'-(3-chloro-4-methylphenyl)-1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinoliny)-N'-(3 ;4-dichlorophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - 1-(7-chloro-4-quinoliny)-N'-(4-cyanophenyl)-5-[(methyloxy)methyl]-1H-pyrazole-4-carbohydrazide ;
 - (3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl phenyl sulfone ;
 - (3-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-5-isoxazolyl)methyl ethyl sulfoxide ;
 - [4-(4-chlorophenyl)-1-(7-chloro-4-quinoliny)-1H-pyrazol-5-yl]methyl methyl ether ;
 - 1-{1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}-3-phenyl-2-propyn-1-one ;
 - N-({1-(7-chloro-4-quinoliny)-5-[(methyloxy)methyl]-1H-pyrazol-4-yl}methyl)-3-(methyloxy)-1-propanamine,

ainsi que leurs éventuelles formes tautomères, leurs sels, N-oxydes et complexes métalliques et métalloïdiques.

35

6. Composés selon l'une quelconques des revendications 1 à 4 de formule générale (IV) :



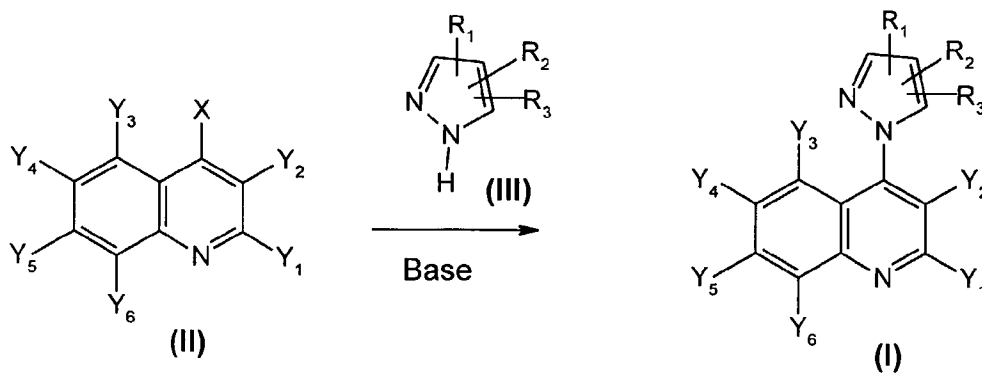
cas particulier des composés de formule (I) pour lesquels R_3 représente l'hydrogène et R_1 et R_2 sont respectivement en position 4 et 5 du noyau pyrazole, R_2 , Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 étant tels que définis dans l'une quelconque des

5 revendications 1 à 4,

et R_1 représente un groupe carboxy, carbamoyle, N-alkylcarbamoyle, N,N-dialkylcarbamoyle, N-alkyl,N-alkoxyalkylcarbamoyle, N-alkoxycarbamoyle, N-alkyl-N-aminoalkylcarbamoyle, N,N-diaminoalkylcarbamoyle, alkoxycarbonyle inférieur; un nitrile, ou un groupe acyle inférieur.

10

7. Procédé de préparation des composés selon l'une des revendications 1 à 6, caractérisé par la réaction :

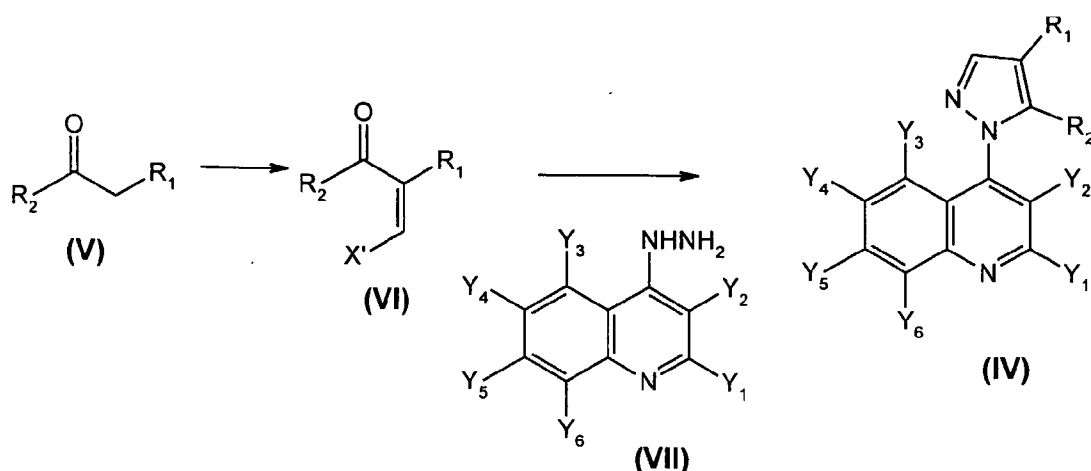


15 formules (I), (II) et (III), dans lesquelles X représente un halogène et R_1 , R_2 , R_3 , Y_1 , Y_2 , Y_3 , Y_4 , Y_5 et Y_6 sont tels que définis dans la revendication 1,

la réaction étant effectuée en présence d'une base organique ou inorganique, en l'absence ou en présence d'un solvant, à une température comprise entre -80°C et

20 180°C ou au point d'ébullition du solvant utilisé.

8. Procédé de préparation des composés selon la revendication 6, caractérisé par la réaction :



où X' représente un atome d'halogène, N,N-dialkylamino ou alkoxy, R_1 , R_2 et Y_1 à Y_6 étant tels que définis pour les composés de formule (IV) ci-dessus.

- 5 **9.** Compositions fongicides comprenant comme matière active une quantité efficace d'au moins un composé selon l'une quelconque des revendications 1 à 6 ou un de ses sels acceptables en agriculture ou un complexe métallique ou métalloïdique de ce composé également acceptable en agriculture.
- 10 **10.** Compositions fongicides selon la revendication 9 comprenant, outre la matière active selon l'une quelconque des revendications 1 à 6 ou un de ses sels acceptables en agriculture ou un complexe métallique ou métalloïdique de ce composé également acceptable en agriculture, un support solide ou liquide, acceptable en agriculture et/ou un agent tensioactif également acceptable en
- 15 agriculture.
- 11.** Compositions fongicides selon l'une des revendications 9 ou 10 comprenant de 0,05 à 95 % en poids de matière active.
- 20 **12.** Procédé de lutte à titre préventif ou curatif contre les champignons phytopathogènes des cultures, caractérisé en ce que les feuilles, les troncs des végétaux ou les sols où poussent ou sont susceptibles de pousser ces végétaux sont traités par application, pulvérisation ou injection d'une quantité agronomiquement efficace et non phytotoxique
- 25 d'au moins un composé selon l'une quelconque des revendications 1 à 6 ou un de ses sels acceptables en agriculture ou un complexe métallique ou métalloïdique de ce composé également acceptable en agriculture ou d'une composition fongicide comprenant une matière active selon l'une quelconque des revendications 1 à 6 et/ou

d'au moins un des composés suivants :

- le *trans*-(+/-)-6-[2-[1-(9-acridinyl)-5-(4-fluorophenyl)-3-(1-méthylethyl)-1*H*-pyrazol-4-yl]ethyl]tetrahydro-4-hydroxy-2*H*-pyran-2-one ;
- le *trans*-(+/-)-6-[2-[1-(9-acridinyl)-5-(4-fluorophenyl)-3-(1-méthylethyl)-1*H*-pyrazol-4-yl]ethenyl]tetrahydro-4-hydroxy-2*H*-pyran-2-one ;
- le 3-méthyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-trifluorométhyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-phenyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-(2-thienyl)-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- les 1-(méthyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;
- les 1-(trifluorométhyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;
- les 1-(phenyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;
- les 1-[(2-thienyl)-quinolin-4-yl]-3-méthyl-5-trifluorométhylpyrazoles ;
- l'endo-1-(7-chloro-4-quinoliny)-5-méthyl-N-(9-azabicyclo[3,3,1]non-3-yl)-1*H*-pyrazole-3-carboxamide ;
- le 5-amino-1-(7-chloro-4-quinoliny)-1*H*-pyrazole-4-carbonitrile ;
- le 4-acetyl-1-(7-chloro-4-quinoliny)-5-méthyl-1*H*-pyrazole ;
- l'acide 5-méthyl-1-(4-quinoliny)-1*H*-pyrazole-4-carboxylique ;
- l'acide 5-cyclopropyl-1-(4-quinoliny)-1*H*-pyrazole-4-carboxylique.

13. Procédé de traitement à titre préventif ou curatif des produits de multiplication des végétaux, ainsi que des végétaux en résultant, contre les maladies fongiques, caractérisé en ce que l'on recouvre lesdits produits d'une quantité efficace et non phytotoxique

de composé ou de composition selon l'une des revendications précédentes et/ou

d'au moins un des composés suivants :

- le *trans*-(+/-)-6-[2-[1-(9-acridinyl)-5-(4-fluorophenyl)-3-(1-méthylethyl)-1*H*-pyrazol-4-yl]ethyl]tetrahydro-4-hydroxy-2*H*-pyran-2-one ;
- le *trans*-(+/-)-6-[2-[1-(9-acridinyl)-5-(4-fluorophenyl)-3-(1-méthylethyl)-1*H*-pyrazol-4-yl]ethenyl]tetrahydro-4-hydroxy-2*H*-pyran-2-one ;
- le 3-méthyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-trifluorométhyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-phenyl-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- le 3-(2-thienyl)-1-(4-méthylquinolin-2-yl)-5-trifluorométhylpyrazole ;
- les 1-(méthyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;
- les 1-(trifluorométhyl-quinolin-4-yl)-3-méthyl-5-trifluorométhylpyrazoles ;

- les 1-(phenyl-quinolin-4-yl)-3-methyl-5-trifluoromethylpyrazoles ;
 - les 1-[(2-thienyl)-quinolin-4-yl]-3-methyl-5-trifluoromethylpyrazoles ;
 - l'endo-1-(7-chloro-4-quinolinyl)-5-methyl-N-(9-azabicyclo[3,3,1]non-3-yl)-1*H*-pyrazole-3-carboxamide ;
 - 5 • le 5-amino-1-(7-chloro-4-quinolinyl)-1*H*-pyrazole-4-carbonitrile ;
 - le 4-acetyl-1-(7-chloro-4-quinolinyl)-5-methyl-1*H*-pyrazole ;
 - l'acide 5-methyl-1-(4-quinolinyl)-1*H*-pyrazole-4-carboxylique ;
 - l'acide 5-cyclopropyl-1-(4-quinolinyl)-1*H*-pyrazole-4-carboxylique.
- 10 **14.** Procédé selon l'une des revendications 12 ou 13 dans lesquelles on traite les céréales, le riz, les arbres fruitiers, les arbres forestiers, la vigne, les cultures oléagineuses, les cultures maraîchères, les solanées ou la betterave.
- 15 **15.** Procédé selon l'une des revendications 12 à 14 dans lesquelles on traite les riz, le blé, l'orge, le seigle, le triticale, les arbres fruitiers, le maïs, le coton, le lin, le colza, la vigne, les arbres forestiers, les pois, les pommes de terre ou la betterave.
- 20 **16.** Procédé selon l'une quelconque des revendications 12 à 15 dans lesquelles on traite le blé ou l'orge.
- 25 **17.** Procédé selon l'une quelconque des revendications 13 à 16 dans lequel on traite les semences de céréales, de pomme de terre, de coton, de pois, de colza, de maïs, de lin ou encore les semences d'arbres forestiers.
- 30 **18.** Procédé selon l'une quelconque des revendications 12 à 17 caractérisé en ce que les plantes sont des plantes génétiquement modifiées.
- 35 **19.** Procédé selon l'une quelconque des revendications 12 à 18 dans lequel la dose de matière active appliquée est comprise entre 10 et 800 g de matière active par hectare, de préférence entre 50 et 300 g de matière active par hectare dans le cas des traitements foliaires.
- 20.** Procédé selon l'une quelconque des revendications 13 à 18 dans lequel la dose de matière active appliquée est comprise entre 2 et 200 g de matière active par 100 kg de semence, de préférence entre 3 et 150 g par 100 kg dans le cas des traitements de semences.

INTERNATIONAL SEARCH REPORT

Internationa | Application No

PCT/FR 00/01816

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D401/04 A01N43/56 C07D491/04 C07D417/14 C07D405/14
 C07D401/14 C07D413/14 C07D409/14 //(C07D491/04, 317:00,
 221:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | <p>CHEMICAL ABSTRACTS, vol. 127, no. 10, 8 September 1997 (1997-09-08) Columbus, Ohio, US; abstract no. 135765q, SINGH, SHIV P. ET AL.: "Reactions of hydrazinoquinolines with trifluoromethyl-beta-diketones: structural and mechanistic studies." XP002133163 abstract & J. FLUORINE CHEM., vol. 83, no. 1, - 1997 pages 73-79, -& DATABASE CHEMICAL ABSTRACTS 'Online! CA 127:135765, XP002133165 composés avec RN 193203-45-1 et - 44-0 --- -/--</p> | 1 |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *8* document member of the same patent family

Date of the actual completion of the international search

24 November 2000

Date of mailing of the international search report

19/12/2000

Name and mailing address of the ISA

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Van Bijlen, H

INTERNATIONAL SEARCH REPORT

Internat: I Application No

PCT/FR 00/01816

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | DE 196 36 509 A (BASF AG) 12 March 1998 (1998-03-12) cited in the application claims ----- | 1,9 |
| A | EP 0 703 234 A (NIHON BAYER AGROCHEM K.K.) 27 March 1996 (1996-03-27) cited in the application page 17, line 20 - line 24; claim 1 ----- | 1,9 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/FR 00/01816

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|------------------------------|--------------------------|
| DE 19636509 A | 12-03-1998 | NONE | |
| EP 703234 A | 27-03-1996 | JP 8143407 A US 5622914 A | 04-06-1996 22-04-1997 |

RAPPORT DE RECHERCHE INTERNATIONALE

Demar ternationale No
PCT/FR 00/01816

A. CLASSEMENT DE L'OBJET DE LA DEMANDE

CIB 7 C07D401/04 A01N43/56 C07D491/04 C07D417/14 C07D405/14
C07D401/14 C07D413/14 C07D409/14 //(C07D491/04,317:00,
221:00)

Selon la classification internationale des brevets (CIB) ou à la fois selon la classification nationale et la CIB

B. DOMAINES SUR LESQUELS LA RECHERCHE A PORTE

Documentation minimale consultée (système de classification suivi des symboles de classement)

CIB 7 C07D A01N

Documentation consultée autre que la documentation minimale dans la mesure où ces documents relèvent des domaines sur lesquels a porté la recherche

Base de données électronique consultée au cours de la recherche internationale (nom de la base de données, et si réalisable, termes de recherche utilisés)

CHEM ABS Data

C. DOCUMENTS CONSIDERES COMME PERTINENTS

| Catégorie ° | Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents | no. des revendications visées |
|-------------|--|-------------------------------|
| X | CHEMICAL ABSTRACTS, vol. 127, no. 10, 8 septembre 1997 (1997-09-08) Columbus, Ohio, US; abstract no. 135765q, SINGH, SHIV P. ET AL.: "Reactions of hydrazinoquinolines with trifluoromethyl-beta-diketones: structural and mechanistic studies." XP002133163 abrégé & J. FLUORINE CHEM., vol. 83, no. 1, - 1997 pages 73-79, -& DATABASE CHEMICAL ABSTRACTS 'en ligne! CA 127:135765, XP002133165 composés avec RN 193203-45-1 et - 44-0 --- -/-- | 1 |

☒ Voir la suite du cadre C pour la fin de la liste des documents

☒ Les documents de familles de brevets sont indiqués en annexe

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- *Z* document qui fait partie de la même famille de brevets

Date à laquelle la recherche internationale a été effectivement achevée

24 novembre 2000

Date d'expédition du présent rapport de recherche internationale

19/12/2000

Nom et adresse postale de l'administration chargée de la recherche internationale

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Fonctionnaire autorisé

Van Bijlen, H

C.(suite) DOCUMENTS CONSIDERES COMME PERTINENTS

| Catégorie | Identification des documents cités, avec, le cas échéant, l'indication des passages pertinents | no. des revendications visées |
|-----------|--|-------------------------------|
| A | DE 196 36 509 A (BASF AG) 12 mars 1998 (1998-03-12) cité dans la demande revendications --- | 1,9 |
| A | EP 0 703 234 A (NIHON BAYER AGROCHEM K.K.) 27 mars 1996 (1996-03-27) cité dans la demande page 17, ligne 20 - ligne 24; revendication 1 ----- | 1,9 |

RAPPORT DE RECHERCHE INTERNATIONALE

Renseignements relatifs aux membres de familles de brevets

Deman internationale No

PCT/FR 00/01816

| Document brevet cité au rapport de recherche | Date de publication | Membre(s) de la famille de brevet(s) | Date de publication |
|---|------------------------|---|--------------------------|
| DE 19636509 A | 12-03-1998 | AUCUN | |
| EP 703234 A | 27-03-1996 | JP 8143407 A US 5622914 A | 04-06-1996 22-04-1997 |